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THE REACTION OF ACTIVE NITROGEN WITH ETHYLENE[1]

BY J. VERSTEEG[2] AND C. A. WINKLER

ABSTRACT

Reinvestigation of the active nitrogen–ethylene reaction has confirmed hydrogen cyanide as the principal product. Smaller quantities of ethane, cyanogen, acetylene, and methane have also been found and the variations in amounts of these products with ethylene flow rate have been established. No significant amount of polymeric material was found.

The reaction of active nitrogen with ethylene has been investigated previously in this laboratory (3) but under conditions such that the results were rendered quantitatively uncertain by the formation of considerable amounts of unidentified polymer. Further experience with reactions of similar type (1) has made it possible to reduce the extent of polymer formation to negligible proportions. The ethylene reaction has therefore been reinvestigated with the improved technique to establish the essential features of the reaction on a more reliable quantitative basis, and to provide a more detailed examination of the reaction products.

EXPERIMENTAL

The apparatus and procedure were identical in all essentials with those used in the earlier studies mentioned above. Formation of the troublesome hydrogen cyanide polymer encountered previously was very largely prevented by eliminating water vapor from the system, and by careful sublimation of the cyanide below its melting point from the main product trap into a bulb containing calcium chloride.

Hydrogen cyanide was estimated both by weight and by titration (6). Cyanogen was determined by alkaline hydrolysis followed by determination of the resulting cyanide (7). A hydrocarbon fraction which was separated cleanly from hydrogen cyanide and cyanogen by distillation at 116° C. was analyzed for acetylene and ethylene by absorption in the manner described by Brooks *et al.* (2). The residual gas was assumed to be ethane. Small amounts of C_3 hydrocarbon might also have been present, although no indication of them was obtained in Podbielniak distillations of three of the hydrocarbon fractions. Also, an average carbon balance of 95% to 96% was obtained, disregarding carbon not accounted for in traces of polymer that were formed

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the Defence Research Board. Permission of the Defence Research Board to publish this paper is gratefully acknowledged.
[2] *Holder of a Research Council of Ontario Scholarship.*

and in possible C_3 or higher hydrocarbons. (The carbon balance in the previous study of the reaction was of the order of 70%.) Methane was determined by combustion over the cupric oxide – ferric oxide catalyst of Brooks *et al.* (2).

RESULTS AND DISCUSSION

The results of the study have been summarized in Fig. 1. The curve for hydrogen cyanide production confirms the main feature of the reaction observed in the previous study; the remainder of the curves represent new information.

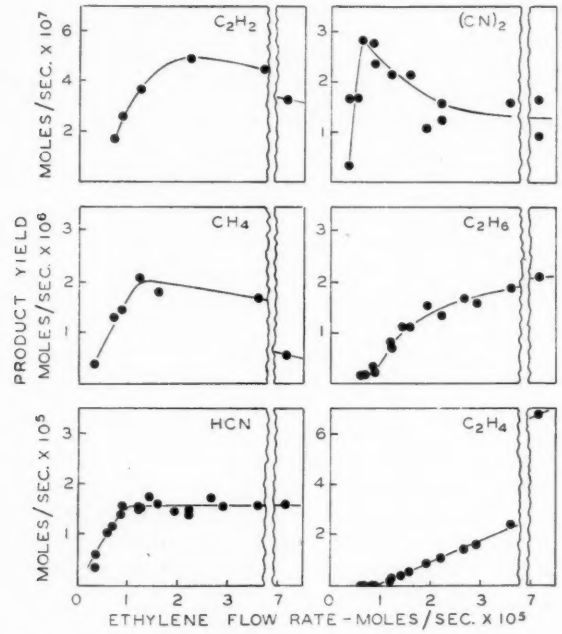

FIG. 1. Rate of formation of various products in the ethylene – nitrogen atom reaction, as a function of the ethylene flow rate.

The present study in itself would not seem to demand serious revision of the earlier reaction mechanism, which assumed as a primary step

$$C_2H_4 + N \rightarrow HCN + CH_3^{\cdot}.$$

However a recent study of the nitrogen atom reaction with propylene (5) has given strong indication that the ethylidene radical is formed in the initial step of that reaction, thus

$$C_3H_6 + N \rightarrow CH_3\,CH{:} + CH_2N$$
$$\downarrow$$
$$HCN + H\,.$$

The analogous reaction with ethylene, though less favorable energetically

than that to form the methyl radical, would lead to the primary production of the methylene radical,

$$C_2H_4 + N \rightarrow CH_2{:} + CH_2N$$
$$\downarrow$$
$$HCN + H\,.$$

No decision between the two possibilities would yet seem possible.

The production of ethane and methane can be reasonably accounted for by reactions of atomic hydrogen with ethylene, and either methyl or methylene radicals, respectively. The observed increase in amount of ethane and decrease in amount of methane with increased flow rate of ethylene presumably correspond to the increasingly preferred reaction of hydrogen atoms with ethylene at the expense of methane formation.

Formation of the observed small amounts of acetylene, and the decrease in these amounts with increased ethylene flow, may be explained by some dehydrogenation of ethylene according to the reactions (cf. 4, p. 262)

$$C_2H_4 + H \rightarrow C_2H_3 + H_2\,,$$
$$C_2H_3 + H \rightarrow C_2H_2 + H_2\,.$$

The formation of cyanogen, with a maximum value at approximately the ethylene flow rate beyond which ethylene is in excess of the nitrogen atoms (determined from hydrogen cyanide production), would seem to be best explained by the reactions

$$C_2H_4 + N \rightarrow [C_2H_4N]^*,$$
$$[C_2H_4N]^* + N \rightarrow [C_2H_4N_2]^*,$$
$$[C_2H_4N_2]^* \rightarrow C_2N_2 + 2H_2\,.$$

This implies that the collision complex is sufficiently stable to suffer an appreciable number of collisions with a second nitrogen atom. The high rate at which ethylene is attacked by atomic nitrogen, compared with, say, the relatively slow attack on ethane (1), makes it seem reasonable to attribute comparative ease of formation and correspondingly significant stability to the ethylene – nitrogen atom complex.

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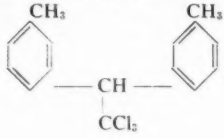
ON THE OXIDATION OF 1,1,1-TRICHLORO-2,2-*BIS*-(*p*-TOLYL)-ETHANE[1]

BY YVON PERRON

ABSTRACT

The condensation of benzene with chloral hydrate in the presence of concentrated sulphuric acid gave rise to 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane. The oxidation of this condensation product with potassium dichromate in dilute sulphuric acid at the boiling temperature yielded 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene, the structure of which was shown by its oxidative degradation to 4,4'-dicarboxybenzophenone. When the oxidation of the same condensation product was carried out in the cold, with the aid of chromium trioxide in glacial acetic acid and acetic anhydride, 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane was obtained in a good yield. This last compound was converted to the dichloroethylenic-dicarboxylic acid upon refluxing with a methanolic solution of sodium hydroxide. The corresponding amide derivatives of both the dichloro and trichlorodicarboxylic acids were also prepared.

In connection with the syntheses of some DDT analogues, 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane and its amide derivative were needed. Haskelberg and Lavie (2) have previously reported the synthesis of this trichlorodicarboxylic acid. According to their procedure, chloral hydrate was first condensed with toluene, as described earlier by Fischer (1), and 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane (I) was obtained.



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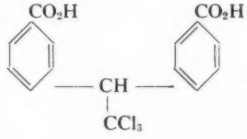
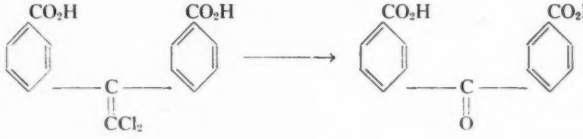


II

This compound was in turn oxidized with the aid of potassium dichromate and dilute sulphuric acid at the boiling point of the mixture. These authors claimed to have obtained by this procedure a 20% yield of 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (II). However, all attempts to prepare this trichlorodicarboxylic acid by the procedure described have failed in our hands. It seemed that under such a drastic condition of oxidation, as employed by these authors, there was, together with the conversion of the methyl groups to carboxyl groups, a concurrent loss of a molecule of hydrogen chloride and the product so obtained was 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene (III).

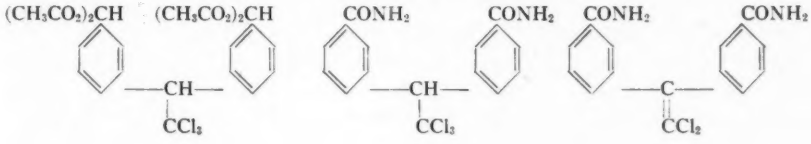


III IV

[1] *Manuscript received October 6, 1952.*
Contribution from the Department of Chemistry, University of Montreal, Montreal, Que.

That the compound obtained, when the procedure described by Haskelberg and Lavie was followed, had really Structure III was shown by elemental analyses and also by the fact that on further oxidation with chromic anhydride in glacial acetic acid at the boiling point of the solvent, it gave rise to 4,4′-dicarboxybenzophenone (IV).

In view of this result a modified method for the preparation of the dicarboxylic acid II was desirable, and in this respect, the oxidation of 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane under milder conditions was attempted.



V VI VII

We have previously reported (4) that Compound I in glacial acetic acid and acetic anhydride, when oxidized at 5° C. with chromium trioxide, gave rise to the tetraacetate of 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (V). The same reaction was carried out at 15° C. instead of 5° C., and under this condition a good yield of the desired trichlorodicarboxylic acid (II) was obtained. Furthermore, we have found that the omission of acetic anhydride from the reaction mixture led to the ethylenic-dicarboxylic acid (III).

1,1,1-Trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (II), upon refluxing with a methanolic solution of sodium hydroxide, was converted to the ethylenic-dicarboxylic acid (III), the melting point of which was undepressed upon admixture with the dicarboxylic acid obtained by the procedure described by Haskelberg and Lavie. The dicarboxylic acids II and III, heated under reflux with thionyl chloride and then treated with concentrated aqueous ammonia, gave rise respectively to 1,1,1-trichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethane (VI) and 1,1-dichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethylene (VII).

EXPERIMENTAL

1,1,1-Trichloro-2,2-bis-(p-tolyl)-ethane (I)

This product was prepared according to Fischer (1).

In a 250 ml. round-bottomed flask, equipped with a mechanical stirrer and a thermometer, chloral hydrate (41 gm.) and toluene (50 gm.) were introduced. The reaction flask was immersed in an ice-bath and the mixture was cooled to 5° C. To this mixture which was mechanically stirred, concentrated sulphuric acid (150 gm.) was added dropwise from a dropping funnel. The stirring was continued for three hours, at room temperature, after the addition of acid had been completed. A semisolid product separated from the reaction mixture. The contents of the reaction flask was poured on crushed ice, and the solid was filtered off and washed thoroughly with cold water to get rid of the excess chloral and sulphuric acid. It was then freed from excess toluene by

trituration with ethanol (50 ml). The crude product was finally recrystallized from 95% ethanol, from which white platelets, m.p. 89° C., were obtained. Yield, 58%.

Oxidation with Potassium Dichromate and Sulphuric Acid

The oxidation of 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane with potassium dichromate and sulphuric acid was carried out as described by Haskelberg and Lavie (2).

Potassium dichromate (38.3 gm.), 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane (13.3 gm.), and water (75 cc.) were introduced into a 500 ml. reaction flask. To this mixture sulphuric acid (85 gm.) was added slowly with stirring. When half of this quantity was added the mixture was heated to the boiling point and the addition was continued at the boiling temperature. The reaction mixture was allowed to cool and it was then poured into 1 liter of cold water. The solid material was collected by filtration and ground with 5% sulphuric acid (150 cc.). The precipitate was filtered off, washed with cold water, and extracted with a 5% aqueous sodium hydroxide solution (100 cc.). The alkaline solution was freed from insoluble residue by filtration and then acidified with a 10% sulphuric acid solution. The precipitated dicarboxylic acid was dissolved in boiling 50% aqueous ethanol and the resulting solution was decolorized with charcoal. After many recrystallizations from that solvent, 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene separated as colorless needles melting at 278° C. (dec.). Yield, 22%. Calc. for $C_{16}H_{10}O_4Cl_2$: C, 56.97; H, 2.96; Cl, 21.06%; neut. equiv., 337. Found: C, 56.88; H, 2.97; Cl, 21.15%; neut. equiv., 339.

1,1,1-Trichloro-2,2-bis-(p-carboxyphenyl)-ethane (II)

1,1,1-Trichloro-2,2-*bis*-(*p*-tolyl)-ethane (15 gm.), acetic anhydride (125 cc.), and glacial acetic acid (125 cc.) were introduced in a 500 ml. reaction flask equipped with a mechanical stirrer and a thermometer. The resulting solution was cooled to 15° C. and concentrated sulphuric acid (25 cc.) was added slowly, from a dropping funnel, with cooling and stirring. After the addition of acid had been completed, the solution was allowed to cool again to 15° C. Chromic anhydride (25 gm.) was then added, in small portions, at such a rate that the temperature did not rise above 20° C. The contents of the reaction flask was kept stirred over a period of 30 min. after all the chromium trioxide had been added. The reaction mixture was then poured on crushed ice. This caused the separation of a brown precipitate which was collected by filtration and subsequently washed with small quantities of cold water until the washings were colorless. The solid was extracted at room temperature with a 2% sodium hydroxide solution (200 cc.) and the insoluble material was removed by filtration. The resulting aqueous solution was acidified with 10% sulphuric acid (100 cc.) which caused the precipitation of the organic diacid. The crude material was filtered off, washed several times with small quantities of cold water, and recrystallized from 75% aqueous dioxane or 50% aqueous ethanol. After three recrystallizations, there was obtained a white crystalline product melting at 283° C. (dec.). Yield, 75%. Calc. for $C_{16}H_{11}O_4Cl_3$: C, 51.48; H,

2.90; Cl, 28.51%; neut. equiv., 373.5. Found: C, 51.45; H, 2.96; Cl, 28.45%; neut. equiv., 374.

1,1-Dichloro-2,2-bis-(p-carboxyphenyl)-ethylene (*III*)

A mixture of 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (1.5 gm.) and a 7% methanolic solution of sodium hydroxide (25 cc.) was refluxed for 10 hr. The methanol was then distilled off under reduced pressure and the solid residue was dissolved in water (25 cc.). The resulting aqueous solution was acidified with a 10% sulphuric acid solution, which caused the precipitation of the free dicarboxylic acid. The white precipitate was filtered off and washed with small quantities of cold water until the washings were neutral to litmus. It was then dissolved in boiling 50% aqueous ethanol. On cooling, 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene crystallized out as colorless needles. After three recrystallizations from that solvent the product melted at 277–278° C., either alone or in admixture with a sample of the dicarboxylic acid obtained by the dichromate – sulphuric acid oxidation. Calc. for $C_{16}H_{10}O_4Cl_2$: C, 56.97; H, 2.96; Cl, 21.06%; neut. equiv., 337. Found: C, 56.90; H, 2.98; Cl, 21.10%; neut. equiv., 338.

4,4'-Dicarboxybenzophenone (*IV*)

Chromic anhydride (1 gm.) and 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene (0.7 gm.) were dissolved in glacial acetic acid (40 cc.). The resulting solution was refluxed gently for two hours after which time the contents of the reaction flask was poured into cold water (100 cc.). This caused the precipitation of the expected ketone. The precipitate was filtered off and washed thoroughly with cold water, until the washings were colorless. After recrystallization from a large volume of 95% ethanol the product was obtained as colorless microcrystalline needles melting over 360° C. (dec.) as reported previously by Limpricht (3). Yield 50%. Calc. for $C_{15}H_{10}O_5$: C, 66.67; H, 3.70%; neut. equiv., 270. Found: C, 66.49; H, 3.81%; neut. equiv., 270.

1,1,1-Trichloro-2,2-bis-(p-carboxamidophenyl)-ethane (*VI*)

A mixture of 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (2 gm.) and freshly distilled thionyl chloride (15 cc.) was heated under reflux for three hours, after which time the solid material had completely dissolved. The unreacted thionyl chloride was distilled off and the residual yellow oil dissolved in ether. The ethereal solution was added cautiously from a dropping funnel, to a concentrated aqueous ammonia solution. This caused the separation of a yellowish precipitate which was removed by filtration and subsequently washed with cold water. The crude 1,1,1-trichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethane thus obtained was recrystallized from methanol, from which it separated as colorless plates, melting at 261–62° C. (dec.). Yield, 90%. Calc. for $C_{16}H_{13}O_2N_2Cl_3$: C, 51.68; H, 3.49; Cl, 28.66; N, 7.53%. Found: C, 51.59; H, 3.52; Cl, 28.60; N, 7.48%.

1,1-Dichloro-2,2-bis-(p-carboxamidophenyl)-ethylene (*VII*)

This amide was prepared exactly as described above for 1,1,1-trichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethane. The product so obtained was recrystallized from methanol from which it separated as colorless rectangular plates

melting at 256–57° C. Yield, 95%. Calc. for $C_{16}H_{12}O_2N_2Cl_2$: C, 57.31; H, 3.58; Cl, 21.19; N, 8.35%. Found: C, 57.26; H, 3.63; Cl, 21.24; N, 8.38%.

ACKNOWLEDGMENTS

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N-BENZOYLPHENYLHYDROXYLAMINE AS A REAGENT FOR TIN[1]

By D. E. Ryan and G. D. Lutwick

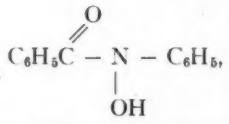
ABSTRACT

N-Benzoylphenylhydroxylamine precipitates tin quantitatively from stannic chloride solutions; complete precipitation is obtained in solutions varying from 1 to 8% in concentrated hydrochloric acid. The reagent reduces stannic to stannous tin before forming the addition compound $(C_{13}H_{11}O_2N)_2\ SnCl_2$; this compound is stable and may be used as a weighing form for tin. Tin can be determined readily in brasses; copper, lead, and zinc do not interfere.

INTRODUCTION

The gravimetric methods for the determination of tin all require ignition to stannic oxide; the oxide, in addition to the disadvantage of a high conversion factor, must be heated to a high temperature and has a marked tenacity for water. The present investigation was undertaken in the attempt to find a reagent that would precipitate a complex from stannic solutions that could be dried at 110°C.

Of 25 compounds tested in preliminary experiments the N-benzoyl derivative of phenylhydroxylamine,



seemed to offer the greatest possibilities. It reacted with stannic chloride solutions to give complete precipitation of the tin and the resulting compound was stable with a melting point of 171°C. This paper is a report on the use of N-benzoylphenylhydroxylamine as a reagent for tin.

EXPERIMENTAL

Preparation

N-Benzoylphenylhydroxylamine was prepared by reacting benzoyl chloride with phenylhydroxylamine following the method of Bamberger (2). However, in the precipitation of the N-benzoyl derivative from ammonia (in which the monobenzoyl compound is dissolved to separate it from any dibenzoyl that may have been formed during the reaction) Bamberger neutralized by means of sulphuric acid. It was found that, because of oxidation and heat of reaction, the neutralized solution was distinctly yellow in color and contained, in addition to precipitated reagent, a reddish brown oil that solidified, contaminating the desired product.

The use of 3*N* hydrochloric acid to neutralize the ammonia resulted in a colorless solution and eliminated the formation of the oil. One recrystallization from hot water gave a white crystalline product with a melting point of 121° C. In recrystallizing from hot water, since prolonged heating caused some decompo-

[1] *Manuscript received August 11, 1952.*
Contribution from the Department of Chemistry, Dalhousie University, Halifax, N.S., with financial assistance from the National Research Council.

sition, 0.6 gm. of the reagent was added for each 100 ml. of boiling water and the solution, after being filtered, was cooled in an ice bath.

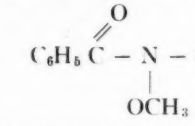
Properties

N-Benzoylphenylhydroxylamine is a white crystalline solid melting at 121° C. It is only slightly soluble in water at 25° C., the solubility being 0.04 gm. per 100 ml.; the solubility in hot water is approximately 0.5 gm. per 100 ml. The reagent reacts much the same as does cupferron but it is more stable towards heat, light, and air; it has been used by Shome (3) to precipitate iron, copper, aluminum, and titanium but the complexes are more easily decomposed by acids than the cupferron derivatives. Reaction occurs, in these compounds, by replacement of the hydrogen of the oxime by the metal and co-ordination to the oxygen of the carbonyl grouping; such is not the case with tin, however, in which an addition rather than an inner complex compound is formed.

Nature of Reaction

The precipitated benzoylphenylhydroxylamine tin compound was found to contain 19.28% tin and 11.3% chlorine; the theoretical percentages for a compound having the composition $(C_{13}H_{11}O_2N)_2SnCl_2$ are 19.27 for tin and 11.5 for chlorine. The hydroxylamine apparently reduces stannic to stannous tin before forming the addition compound; complexes precipitated from stannous and stannic chloride solutions have the same composition with a melting point of 171° C.

That the metal is not linked to the oxygen and the hydrogen of the oxime plays no part other than that of reducing the stannic tin is shown by the ready formation of similar compounds by the O-methyl ether of benzoylphenylhydroxylamine,



with stannous chloride solutions; no reaction occurs with stannic chloride solutions.

Methods

1. *Ignition to the Oxide*

To aliquots of a standard solution of stannic chloride were added varying amounts of concentrated hydrochloric acid and the solutions were diluted to 100 ml. Three milliliters of a 10% solution of benzoylphenylhydroxylamine in ethyl alcohol was added slowly, with stirring. The solutions were then cooled in an ice bath for one hour and the precipitates were filtered through S & S No. 589 white ribbon filter paper, washed with ice water, and ignited to the oxide. The results are shown in Table I.

Table I shows that tin can be quantitatively precipitated by means of benzoylphenylhydroxylamine from solutions varying from 1 to 8% in concentrated hydrochloric acid. Incomplete precipitation at higher concentrations of the acid is neither caused by an increase in the stability of $SnCl_6''$ with increasing chloride ion concentration nor by failure of reduction to take place; complete precipitation was obtained from solutions 15% in chloride (from sodium chloride) while only

TABLE I

PRECIPITATION OF TIN BY BENZOYLPHENYLHYDROXYLAMINE AND SUBSEQUENT WEIGHING AS THE OXIDE

Tin taken, mgm.	Tin recovered, mgm.	Remarks
9.45	9.45	Solution 1% in concentrated HCl
9.45	9.45	Solution 1% in concentrated HCl
9.45	9.38	Solution 5% in concentrated HCl
9.45	9.45	Solution 5% in concentrated HCl
9.45	9.35	Solution 8% in concentrated HCl
9.45	9.45	Solution 8% in concentrated HCl
8.34	8.03	Solution 10% in concentrated HCl
9.76	9.77	Tin determined in brass sample after dissolving approximately 0.1 gm. of the brass in concentrated HCl and a few drops of HNO_3
11.09	11.11	Tin determined in brass sample after dissolving approximately 0.1 gm. of the brass in concentrated HCl and a few drops of HNO_3
12.5	12.4	Sample of $(Et_3N)_4\ SnCl_4$ analyzed for tin
33.0	33.3	Sample of $(EtNH_2)_6\ SnCl_4$ analyzed for tin
25.8	26.2	Sample of $(Et_3N)_2\ SnCl_4$ analyzed for tin

slight precipitation was obtained from stannous solutions 15% in concentrated hydrochloric acid.

Although copper can be quantitatively precipitated by benzoylphenylhydroxylamine at pH 3.6 – 6.0, no interference was encountered from copper, lead, or zinc in precipitating tin from brass solutions containing 7% of concentrated hydrochloric acid. Copper was determined successfully in the filtrates from the tin precipitation, after neutralizing with ammonia, by the method of Shome (3).

The tin addition compounds were prepared by W. R. Trost (4) and were analyzed by dissolving the compounds in 5% hydrochloric acid and following the usual procedure.

2. *Weighing as the Complex*

To aliquots of a standard solution of stannic chloride were added 10 ml. of concentrated hydrochloric acid and the solutions were diluted to approximately 200 ml. From a separatory funnel was added, dropwise and with stirring, 5 ml. of a 1% solution of the reagent in alcohol for each 10 mgm. of tin present plus 8 ml. in excess. The solutions were cooled in an ice bath for four hours, the precipitates filtered on a filter crucible, washed with a few milliliters of ice water, and dried at 110° C. The weight of the precipitate was multiplied by the theoretical factor 0.1927 to obtain the weight of tin. Results are shown in Table II.

It is essential that the reagent concentration be closely regulated because of the slight solubility of the reagent and the necessity of excess reagent for complete precipitation. The first four results in Table II were obtained by adding 225 ml. of a saturated aqueous solution of the reagent to precipitate the tin; to avoid the addition of the large volume necessary for greater quantities of tin a 1% solution of the reagent in ethyl alcohol was found to be satisfactory and all other results were obtained using the above procedure.

TABLE II

PRECIPITATION OF TIN BY BENZOYLPHENYLHYDROXYLAMINE AND WEIGHING AS THE COMPLEX $(C_{13}H_{11}O_2N)_2\ SnCl_2$

Tin taken, mgm.	Tin recovered, mgm.	Tin taken, mgm.	Tin recovered, mgm.
4.79	4.78	4.57	4.60
4.79	4.74	10.02	9.98
4.79	4.80	10.02	10.03
4.79	4.78	11.50	11.54
4.57	4.60	*11.50	11.45
4.57	4.51	23.00	23.08
4.57	4.57	*23.00	23.01
4.57	4.59		

**These results were obtained, independently, by a member of this laboratory.*

DISCUSSION

Cupferron and neocupferron (the ammonium salts of nitrosophenyl and nitrosonaphthyl hydroxylamine respectively) react with stannous and stannic tin by replacement of the hydrogen of the oxime grouping to give complexes of the type SnC_2 and SnC_4 (1). That the N-benzoyl derivative of phenylhydroxylamine does not behave similarly but forms an addition compound can probably be attributed to its greater basicity. The fact that the replacement of the hydrogen of the oxime does not occur with tin is important; it suggests the possibility of preparing reagents that will permit separations from elements that do require the presence of a replaceable hydrogen for reaction. Thus the O-methyl ether of benzoylphenylhydroxylamine reacts with tin (II) and antimony (III) but does not react with iron or copper. Further investigations of N-benzoylphenylhydroxylamine for separating and determining tin have been discontinued, for the present, in order to investigate more fully these possibilities.

ACKNOWLEDGMENTS

We take this opportunity to thank Mr. L. S. Theobald (Imperial College, London), who suggested this problem to one of us, and Dr. W. J. Chute, who co-operated in the preparation of various organic compounds.

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KINETIC STUDIES OF A REDOX POLYMERIZATION[1]

By R. M. Brown[2] and C. A. Winkler

ABSTRACT

Kinetic studies of a redox-initiated polymerization have indicated activation energies of 9.7 kcal. per mole for the decomposition of the initiating system, approximately 6 kcal. per mole for the propagation reaction, and 9.0 kcal. per mole for the consumption of MTM-4 in the emulsion system. Lower polymerization temperatures raised the gel point without shortening the polymer chains, apparently by decreasing the proportion of cross-linking to propagation reactions. Two types of nonmercaptan termination have been found to occur to appreciable extents: mutual termination of free radicals and a termination process involving the emulsifier.

INTRODUCTION

The introduction of low temperature redox polymerization systems has improved significantly the physical properties of synthetic elastomers (5, 19, 21). The improvement may be ascribed to increased regularity in configuration of the polymer chains (2, 7, 9, 12, 15). The present paper describes some experiments in which the effect of temperature on several aspects of the reaction kinetics has been examined, using a typical redox polymerization recipe.

EXPERIMENTAL

The standard bottle technique for emulsion polymerization (13) was used, with end-over-end rotation at 35 r.p.m. in a water bath controlled to ± 0.02°C. The polymerization recipe was slightly modified from one of Mitchell, Spolsky, and Williams (16), and consisted of:

Component	Parts by weight
Butadiene*	75.0
Styrene*	25.0
Cumene hydroperoxide* (68%)	0.24
Dresinate 731* (dry wt.)	4.70
Sodium hydroxide	0.11
Mixed tertiary mercaptan* (MTM-4)	Variable (0.00 to 0.20)
Kalex sodium* (dry wt.)	0.15
Dextrose	0.50
$FeSO_4.7H_2O$	0.028
$Na_3PO_4.12H_2O$	0.34
Distilled water	180
Di-*tert*-butyl hydroquinone* (shortstop)	0.40

**Kindly donated by Polymer Corporation, Sarnia, Ont.*

The Dresinate 731 emulsifier and the sodium hydroxide were combined in a stock solution. The activator, consisting of an organic complex of ferrous iron

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which was sensitive to oxygen, was prepared in a stock solution by dissolving the sodium phosphate, ferrous sulphate, dextrose, and Kalex sodium in about 20 parts of the water charge and boiling exactly 10 min. The activator solution, when stored under oxygen-free nitrogen, could be kept indefinitely without change in effectiveness.

The shortstop, di-*t*-butyl hydroquinone, was prepared as a suspension using the same emulsifying agent present in the latex.

The components were charged into 1-oz. bottles in the order: water, soap solution, activator solution, styrene solution of mercaptan, styrene solution of cumene hydroperoxide, and, finally, an excess of butadiene, which was allowed to evaporate to the desired weight, to expel air from the bottle.

Analytical Methods

Self-sealing Butyl rubber* gaskets under each bottle cap allowed repeated insertion of a hypodermic needle for purposes of injecting shortstop or withdrawing a sample of latex (8). The extent of polymerization was determined on the basis of solids content of the latex (11) correcting for known nonpolymer solids in the recipe.

The residual mercaptan in the latex at any desired conversion was determined by amperometric titration with silver nitrate according to the method of Kolthoff and Harris (14). Satisfactory sampling of the latex for this purpose proved impossible and it was necessary to coagulate and titrate the whole contents of a bottle, except for a 1 ml. sample removed for determination of percentage conversion.

The intrinsic viscosity of the polymer product was measured by determining the flow times of polymer solutions at 24.8°C. in a modified Ubbelohde viscometer having a large solution reservoir to allow measurements at several concentrations by successive dilutions in the viscometer. The vistex method of Henderson and Legge (10) was followed using 80/20 (by volume) toluene–isopropanol as solvent and pure toluene as diluent to obtain the several solutions required for the determination of the kinematic flow time in pure toluene. Since the viscometers were designed with reasonably long flow times, kinetic energy corrections were neglected and results recorded as intrinsic flow times.

RESULTS AND DISCUSSION

The Polymerization Reaction

Persistent difficulty in obtaining a reproducible rate of reaction was encountered in the preliminary work with this polymerization system. No definite cause for this difficulty was identified, but with further experience with the system, reproducibility between individual bottles of a particular experiment of $\pm$ 1.5% conversion was achieved. The rate of polymerization continued to vary from experiment to experiment, but enough polymerizations were observed to give good average values for the polymerization rate under various conditions.

Typical rate curves for the polymerization reaction at various temperatures are plotted in Fig. 1. In contrast to the inhibition period often observed in poly-

*Kindly donated by Polymer Corporation Ltd., Sarnia, Ont.

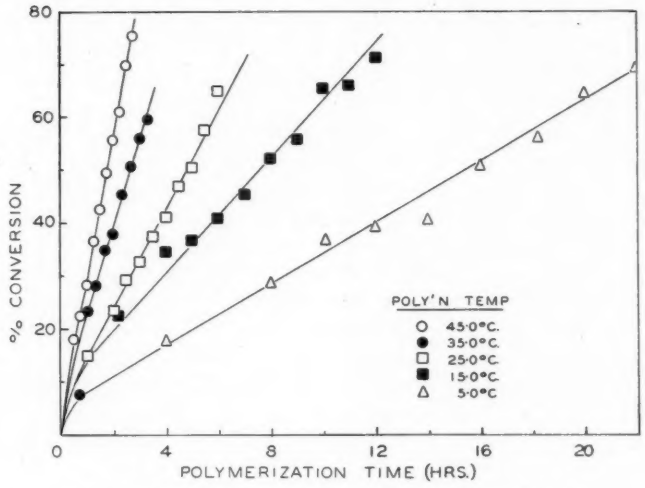

FIG. 1. The rate of polymerization at various temperatures.

merizations of the Mutual recipe system (3), the present system displayed a very fast initial reaction in all experiments. The amount of this initial surge was variable, but usually amounted to an intercept of 6 – 10% conversion when the zero order portion of the rate curve was extrapolated back to zero time. This fast reaction appears to be dependent on the initiating system as a whole, since when either the peroxide, or the activator, or both were omitted from the charge, no polymerization took place at all. If these components were then added to the emulsified charge by syringe, the usual polymerization curve was obtained. The initial surge was unaffected by the elimination of mercaptan from the charge, or substitution of potassium laurate for the Dresinate emulsifier.

The actual consumption of activator during the course of polymerization was slight. Table I indicates that the polymerization rate becomes sensitive to acti-

TABLE I

THE DEPENDENCE OF POLYMERIZATION RATE ON ACTIVATOR CONCENTRATION
Polymerization temperature = 25.0°C
Polymerization time = 5.50 hr.
No mercaptan charged.

Activator (fraction of normal*)	% Conversion
0.25	33.8
0.50	50.5
0.75	55.0
1.00	55.5

**Normal charge refers to that quoted in the polymerization recipe.*

vator concentration at an activator charge below one half of that normally used. In spite of this sensitivity at low activator concentration, a uniform rate of polymerization up to high conversions was observed using one quarter the normal activator charge.

An Arrhenius plot for the average zero order rates of polymerization between 10% and 65% conversion at five different temperatures yielded a value of 9.7 kcal. per mole for the activation energy of the process which is rate controlling during the zero order portion of polymerization. This is of the same order of magnitude as the activation energy of 11.1 kcal. per mole found for the free radical reaction of Fe^{++} and cumene hydroperoxide by Fordham and Williams (6).

The polymerization has been found to become first order in respect of monomer when reaction has proceeded to such an extent that the concentration of monomer becomes the rate-controlling factor, i.e. beyond 65 – 70% conversion. In this region of reaction no separate monomer phase exists, hence the monomer concentration at the site of reaction is given by the total monomer remaining in the system. The rates indicated by the first order plots in Fig. 2 permit an estimate

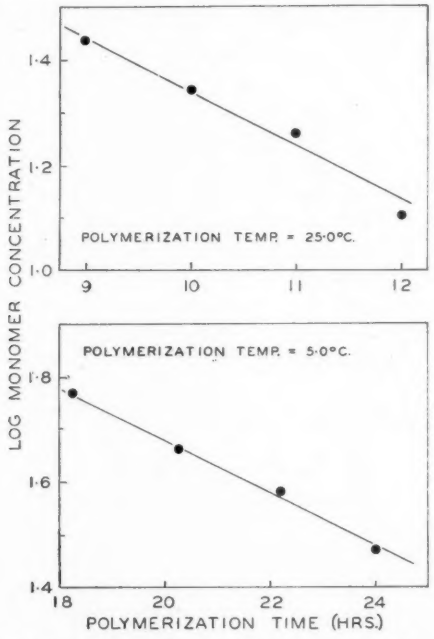

FIG. 2. First order plot of monomer disappearance at high conversions.

of 6 kcal. per mole for the activation energy of the reaction responsible for disappearance of monomer, i.e., the propagation reaction. This value is very approximate since the first order reaction can be followed only over a short range.

Termination Reactions

Typical analytical data for the disappearance of MTM-4 during the course of

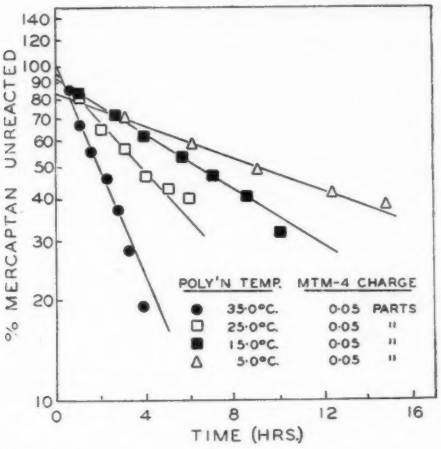

FIG. 3. The rate of mercaptan disappearance at various temperatures.

the polymerization at various temperatures are plotted in Fig. 3. The reaction of MTM-4 as a chain transfer agent in this emulsion showed first order kinetics up to about 60% conversion in a manner similar to the behavior of mercaptans of the Mutual system. However, anomalous behavior was observed during the early stages of reaction. It was found that the rate of mercaptan disappearance did not keep up with the rate of polymerization during the fast initial polymerization. In spite of this, the polymer formed during this stage of reaction was of low molecular weight rather than high. Hence a mode of termination other than by mercaptan would appear to play a major role in the initial stage of polymerization. Higher mercaptan consumption occurred during the initial surge of polymerization, the lower the temperature. This suggests that the nonmercaptan terminating reaction has or is controlled by an activation energy greater than that governing MTM-4 chain transfer. An Arrhenius plot of the zero-time intercepts obtained from a large-scale plot of Fig. 3 indicates a value of about 0.9 kcal. per mole for the activation energy difference of the two terminating processes.

An Arrhenius plot for the first order rate of MTM-4 disappearance at different temperatures gave an activation energy of 9.0 kcal. per mole for the over-all process of MTM-4 consumption. This is not an activation energy for the isolated reaction between the growing free radical and the mercaptan molecule. It is, rather, a measure of the temperature dependence of the over-all process that involves transport of the mercaptan molecule from the oil droplet in the emulsion to the monomer–polymer particle, and its subsequent reaction with the growing free radical.

From this value and the difference in activation energy of the two terminating processes, the second terminating process is found to be controlled by an activation energy of about 9.9 kcal. per mole. This is in reasonable agreement with the value of 9.7 kcal. per mole obtained for the production of free radicals by the

initiating system, as indicated by the polymerization reaction. This suggests that the early nonmercaptan termination is, in reality, mutual termination of free radicals and is controlled by the concentration, hence rate of production, of free radicals in the same sense as the rate of the polymerization reaction itself. The existence of an appreciable amount of mutual termination during the fast initial polymerization is to be expected when it is considered that this fast reaction indicates an abnormally high concentration of initiating and growing free radicals.

Evidence that considerable nonmercaptan termination is operating in this system throughout the course of polymerization is given by a comparison of degrees of polymerization calculated from mercaptan consumption data and from intrinsic viscosity data. In a system in which all termination is by mercaptan chain transfer, the weight average degree of polymerization that would be attained in the total absence of cross-linking and branching reactions may be calculated from mercaptan consumption data as shown by Bardwell and Winkler (1):

$$\bar{y}_{w_\alpha} = 2(e^{r\alpha} - 1)/r^2\alpha R_0,$$

α = fractional extent of conversion of monomer to polymer,
$\bar{y}$ = average degree of polymerization, i.e. average number of structural units per polymer chain,
$\bar{y}_{w_\alpha}$ = weight average degree of polymerization at conversion α,
R_0 = initial mercaptan concentration (as moles per mole of initial monomer),
r = regulating index (4) $= -d \ln R/d\alpha$.

Statistical mechanical considerations relate the various primary degrees of polymerization (1):

$$\bar{y}_v \doteq \frac{1.85}{2.00}\bar{y}_w.$$

Hence, $\bar{y}_v$ for the polymer chains that would be formed in the total absence of branching or cross-linking, i.e. the primary polymer chains, can be evaluated provided all termination is by mercaptan chain transfer. At very low conversions, where the extent of cross-linking is small, the degree of polymerization calculated from viscosity data and from mercaptan consumption data should be of the same order, but the viscosity degree of polymerization should rapidly become larger than the $\bar{y}_v$ calculated from mercaptan disappearance as the reaction proceeds to the gel point.

A comparison of $\bar{y}_v$ calculated from mercaptan consumption data and from intrinsic viscosity data is made in Fig. 4 for a polymerization at 35°C. Molecular weights are calculated from intrinsic viscosity values in toluene using the relation:

$$[\eta] = 5.25 \times 10^{-4} \times M_v^{0.67}$$

which has been established for GR-S polymerized at 50°C. (18). Structural heterogeneity of butadiene–styrene copolymer does not vary greatly with polymerization temperature (15), and this equation should be reasonably valid for polymer formed at 35°C. An average molecular weight of the structural unit of the copolymer of 59.4 has been used to calculate average degrees of polymerization from the viscosity molecular weights.

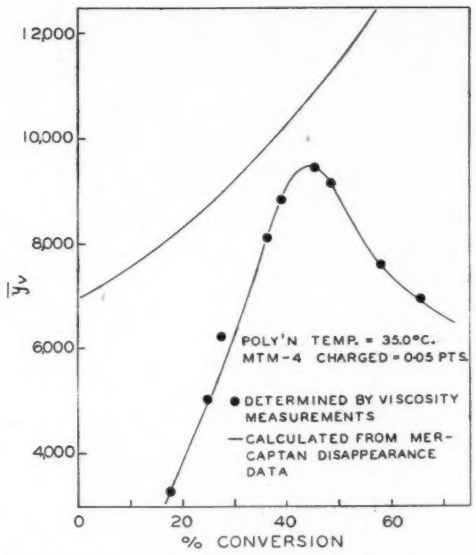

FIG. 4. Comparison of the average degrees of polymerization determined by viscosity measurements, using the equations:

$$[\eta] = 5.25 \times 10^{-4}\, M_v^{0.67},$$
$$\bar{y}_v = M_v/59.4,$$

with those calculated from kinetic data for the disappearance of mercaptan using the equations:

$$\bar{y}_v = 0.92\,\bar{y}_w = 0.92 \times 2(e^{r\alpha} - 1)/\alpha r^2 R_0$$

where $R_0 = 1.39 \times 10^{-4}$ moles mercaptan per mole initial monomer,
$r = 1.88$ for polymerization at 35.0°C. from Figs. 1 and 3.

In Fig. 4, the actual molecular weights indicated by viscosity measurements are seen to be much lower than the primary molecular weights suggested by mercaptan consumption data, in spite of the existence of extensive cross-linking that must be present in the polymer just prior to, and at the gel point. Thus, the mercaptan consumption cannot be a true indication of the primary molecular weights, and extensive termination by other means must occur. Comparison of the molecular weights at low conversion, i.e., 20% conversion, suggests that mercaptan terminates less than half of the polymer chains formed, since the average degree of polymerization calculated from mercaptan consumption data is about twice that indicated by viscosity measurements. Accurate comparisons of this type at very low conversions to obtain quantitative information about the extent of mercaptan termination are precluded in this system by the anomalous behavior of the polymerization and mercaptan chain transfer reaction rate in this region.

The nonmercaptan termination operating during the main course of reaction appears to arise from at least two sources as indicated by investigation of the effect of recipe constituents on the intrinsic viscosity–conversion curve. The nature of the emulsifier and the concentration of the activator have both been found to affect the viscosity–conversion curve (Fig. 5*A*) in such a way as to

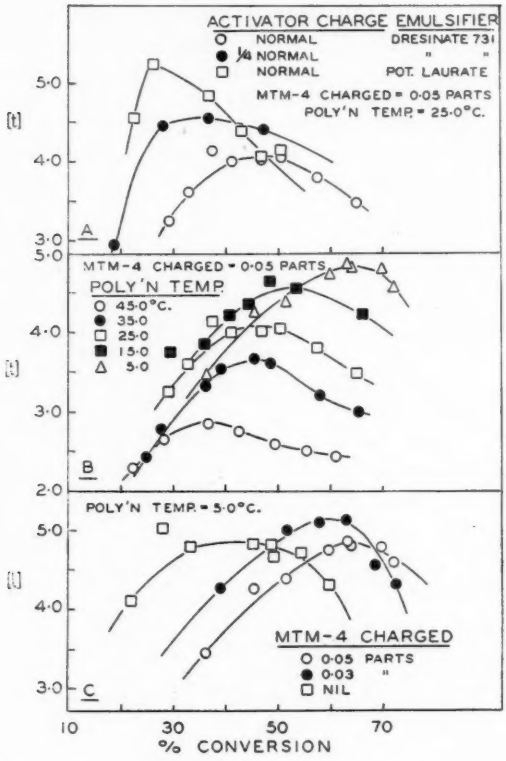

FIG. 5. The effect of polymerization variables on the viscosity–conversion relationship.

indicate clearly that they are responsible for considerable termination in the system. A reduction of the amount of this termination by changing the emulsifier and by reducing the concentration of activator has resulted in lower gel points in a manner analogous to the effect of reduced mercaptan concentration.

The emulsifier probably terminates by a chain transfer mechanism similar to the reaction of mercaptan. The chemical nature of the emulsifier and the fact that polymerization proceeds at a fast rate support this suggestion. If the emulsifier were merely terminating without simultaneously initiating, it would drastically lower the free radical concentration, hence the rate of polymerization.

It is conceivable that some constituent of the activator could act as a chain transfer agent, but it is much more likely that the activator affects the polymer molecular weight by its effect on the free radical concentration in the polymerizing system, i.e., through influencing mutual termination. A lowering of the free radical concentration in the system, such as that produced by a decrease in the activator charge, should reduce the rate of mutual termination relative to the

rate of polymerization since the former depends on $[R^{\bullet}]^2$ whereas the latter is dependent on $[R^{\bullet}]$.

The difference of only 1 kcal. per mole between the activation energies of the processes that are rate controlling for mercaptan chain transfer and mutual termination explains the greater extent of mutual termination in this system than in the persulphate-initiated system. The two termination reactions are allowed to compete on a practically equal basis, and there will always be a relatively large proportion of mutual termination in this system, even in the presence of larger amounts of mercaptan. This makes the calculation of primary molecular weights of redox-produced polymer from mercaptan consumption data a doubtful procedure under the usual conditions of mercaptan concentration.

The Cross-linking Reaction

Further investigation of the viscosity–conversion relationship of polymer produced in this system has given qualitative information about the cross-linking reaction. Since gelation occurs when there is, on the average, one cross-link per primary chain (20), the gel point depends on the number of primary chains, hence on the average primary chain length, as well as on the total number of cross-links in a system. In considering gel point data it is important to distinguish between effects arising from variation of the amount of cross-linking and effects arising from variation of the primary chain length. The intrinsic viscosity of the polymer before and at the gel point is helpful in drawing this distinction.

The viscosity characteristics of the polymer formed in this investigation have been found to be markedly affected by polymerization temperature, as illustrated in Fig. 5*B*. Low temperatures allow the production of soluble polymer up to higher conversions where the kinetics of the termination reactions result in higher primary molecular weights. Below the gel points the relatively small differences in polymer viscosities at the same conversion suggest that the size of the primary polymer chains is comparable for the different polymerization temperatures. This primary polymer chain length is not completely controlled in these polymerizations since both the mutual termination and mercaptan chain transfer reactions are temperature sensitive. In any case a comparison of the viscosities gives only an approximate indication of the relative primary chain lengths, since varying amounts of branching and cross-linking are present in the different polymers, especially close to the gel point.

When the gel point is raised by using a larger amount of chain transfer agent instead of a decrease of temperature, much shorter polymer chains are formed at the same conversion, as indicated by the polymer viscosities below the gel point presented in Fig. 5*C*. The reduction in chain length produced by the additional chain transfer agent is usually sufficient to counteract the effect of increased conversion on the chain length, with the result that the peak of the viscosity–conversion curve is usually lower in spite of the fact that it occurs at higher conversions.

This contrast between the effect of polymerization temperature and concentration of a chain transfer agent is evidence that the reduction in gelation achieved by lowering temperature is a result of a reduction in the amount of cross-linking

and not a result of a decrease in polymer chain length. The fact that this is a temperature effect on the amount of cross-linking suggests that the rate of cross-linking relative to the rate of propagation is decreased with lowering temperature, i.e., the cross-linking reaction has a higher activation energy than the propagation reaction. Morton and Salatiello have observed a similar dependence of gel point on polymerization temperature in the polymerization of butadiene in a Mutual recipe system (17). The quantitative treatment applied by these workers cannot be extended to this redox system because of a mixed nature of the terminating processes operating.

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HYDROXYLATION AND EPOXIDATION OF RAPESEED OIL DERIVATIVES WITH SUBSEQUENT PYROLYSIS AND AMMONOLYSIS[1]

By O. L. Mageli,[2] E. W. Patteson,[3] and E. Y. Spencer[4]

ABSTRACT

A method was developed to follow the hydroxylation of rapeseed oil and erucic acid derivatives with peracetic acid. Peracetic acid prepared *in situ* was found to be equally as effective as the preformed acid in hydroxylation of methyl erucate. Among the compounds synthesized were ethyl 13,14-dihydroxybehenate, methyl 13,14-oxidoerucate, ethyl 13,14-diacetoxybehenate, and methyl 13,14(14,13)-hydroxyacetoxybehenate which were subsequently pyrolyzed at approximately 300° C. with *p*-toluenesulphonic acid as catalyst. The first compound yielded mainly the corresponding ketone with a small amount of the oxido derivative, the chief product of the second compound was also the ketone with some unsaturated material, the third compound yielded 43% of the diene, while the last one yielded 60%. Ammonolysis of the oxido compound or the bromohydrin to yield the corresponding aminohydroxy derivative under pressure with liquid ammonia and ammonium bromide was unsuccessful. A new compound oxidoerucamide, m.p. 101.5°, was synthesized.

INTRODUCTION

The semidrying oil from rapeseed has a high proportion of mono-unsaturated fatty acids and is particularly rich in the glyceride containing the C_{22} fatty acid, erucic acid (22). It appeared, therefore, of interest to study the acids of this oil, and especially erucic acid, to increase their unsaturation or form amino derivatives through the intermediate steps of hydroxylation and epoxidation.

A number of reagents have been used to hydroxylate unsaturated fatty acids. Organic peracids are particularly efficient. Of these performic and peracetic acid are the most useful and offer a number of advantages (19). The use of peracetic acid also allows the isolation of the epoxy or oxirane derivatives of the unsaturated acids (7). Advantage was taken of this to prepare oxidoerucic acid as an intermediate in ammonolysis investigation. The use of both *in situ* and preformed peracids was examined. The preparation of preformed acids is lengthy and loss of active oxygen occurs on storage so that preparation *in situ* was usually employed.

Owing to the variation in time for peracid oxidations to proceed to completion, the rate of peracetic acid oxidation of methyl erucate with and without catalyst was studied. Earlier attempts in this laboratory (13) to follow the hydroxylation by means of iodine numbers using Wijs solution were unsuccessful owing to the difficulty of obtaining representative samples from the heterogeneous reaction mixture and the insolubility of more completely

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hydroxylated material in the Wijs solution. Attempts to determine residual peroxide with ceric sulphate (17) were finally abandoned when it was shown that the rate of decomposition of the peroxide was nonlinear (13). The rate of hydroxylation was finally studied by destruction of unreacted peroxide and peracid with zinc dust and determining the residual unsaturation by employing a modified Rosenmund–Kuhnhenn iodine reagent (2) to overcome the insolubility problem.

Peracid oxidation of unsaturated vegetable oils does not appear to go to completion (18) by contrast with the oxidation of isolated single fatty acid esters. Performic acid oxidation of rapeseed oil triglycerides according to a modified procedure of Greenspan (9) was therefore investigated to determine whether some polymerization occurs during the hydroxylation.

Since the use of peracetic acid allows the production of glycols, oxido compounds, mono and diesterified glycols, pyrolysis of these would indicate the possibility of producing ketones or introducing conjugated diene systems. Crowder and Elm (4) found that pyrolysis of both hydroxyacyloxy and diacyloxy stearic acid as well as the epoxy compound yielded varying amounts of the conjugated diene. This is in agreement with others (14).

With the production of oxidoerucic acid, the possible introduction of an amino group at the center of a C_{22} chain by ammonolysis appeared of interest. Although ethylene and propylene oxide react readily with ammonia, very little work has apparently been done on the epoxides of unsaturated fatty acids. One reaction to introduce nitrogen at the position formerly occupied by the double bond was carried out by Bauer and Bähr (1) by reacting oxidoerucic acid with hydrazine hydrate in a bomb. However no further work along this line has been reported.* The lack of literature, of course, may be due to the relatively unreactive nature of this oxido compound as was demonstrated in this laboratory.

METHODS AND MATERIALS

The rapeseed oil was that obtained by expeller expression. Initially erucic acid was isolated essentially by the method of Dorée and Pepper (5). Later the methyl esters of rapeseed oil were prepared by the method of Hilditch (11) and methyl erucate separated by fractional distillation in a Podbielniak column at 244° C., 10 mm.

Performic Acid Oxidation

Performic acid was prepared *in situ* and both 30% and 90% hydrogen peroxide were employed. The method of performic acid oxidation was essentially that of Greenspan (9). In the preparation of large batches of hydroxylated rapeseed oil acids for the isolation of dihydroxybehenic acid by fractional crystallization, the following method was used: 200 gm. of rapeseed oil acids were added to 600 ml. of 90% formic acid in a three-necked flask. To

**Since the preparation of the original draft of the manuscript a paper has been cited by G. W. Pigulevskii and I. L. Kuranova in Doklady Akad. Nauk. S.S.S.R. 82: 601. 1952, in which the authors outline the synthesis of an aminohydroxy compound derived by the treatment of epoxyoleic acid with aqueous ammonia for 12 hr. at 130° C.*

100 ml. of formic acid were added hydrogen peroxide in 5% excess and enough concentrated sulphuric acid to give a final sulphuric acid content of 1% by weight. The performic acid mixture was then added rapidly to the vigorously-stirred mixture of fatty acids and formic acid. The temperature was maintained at 40° C. for three and one-half hours. Cooling was necessary initially. The hydroxylated fatty acids were separated by addition of water and filtering. To complete the hydrolysis of the formoxy ester and yield the dihydroxy compound, the mixture was heated with *N* sodium hydroxide. After neutralization and washing, 13,14-dihydroxybehenic acid was crystallized several times from dioxane. Normally the lower melting isomer (m.p. 101° C.) was isolated. However in one instance when 5*N* sodium hydroxide was used for hydrolysis, the higher melting hydroxylated acid (m.p. 132–3° C.) was isolated. This was not investigated further in this work.

Peracetic Acid Oxidation

Preformed peracetic acid was used for the oxidation of fatty acids and their esters when it was desired to isolate the epoxy derivatives. The peracetic acid solution was prepared by the method of Swern, Findley, and Scanlan (21).

Oxidations with peracetic acid prepared *in situ* were carried out according to the method of Swern *et al.* (20). The amount of hydrogen peroxide employed was calculated on the basis of 1.2 moles per mole of unsaturation. Glacial acetic acid and hydrogen peroxide were used in the ratio of 20: 1.

Contrary to the statements of Greenspan (9) and Swern *et al.* (21) to the effect that the hydroxyacetoxy compounds could be isolated in high yields using this procedure, the chief product isolated was identified as the dihydroxy compound both by melting point and hydroxyl value.

The method of Greenspan and MacKellar was used to standardize peracetic acid solution in the presence of hydrogen peroxide using ceric sulphate (10).

The rate of peracetic acid hydroxylation was determined by removing quantitatively a 2 ml. sample of the rapidly-stirred reaction mixture from a three-necked flask maintained at constant temperature. The sample was then transferred to a 15 ml. centrifuge tube containing 10 ml. of dioxane. Two to three grams of zinc dust were added, the tube corked, shaken thoroughly, and allowed to stand for one hour with intermittent shaking. The mixture was then centrifuged and a 2 ml. sample was removed from the supernatant liquid for an iodine number determination by the modified Rosenmund–Kuhnhenn method (2).

Epoxy oxygen was determined by the method of Findley *et al.* (6) based on the quantitative consumption of hydrogen chloride required to open the oxirane ring.

Hydroxyl values were estimated by the acetic anhydride – pyridine method of Ogg *et al.* (15).

Carbonyl oxygen was determined by the potentiometric method of Knight and Swern (12) using hydroxylamine. Rinsing down the flask with water toward the end of the titration, as suggested, altered the pH considerably.

The use of aldehyde-free ethanol was found to be more suitable. The hydroxylamine reagent when prepared with aldehyde-free ethanol and stored in the refrigerator was stable up to four days and thus its daily preparation was not necessary.

Unsaturation was originally determined by the Wijs iodine–chloride method. However, it was later replaced by the Rosenmund–Kuhnhenn method as modified by Benham and Klee (2). By the use of mercuric acetate catalyst complete addition to conjugated systems was obtained.

Conjugated dienes were also determined by ultraviolet absorption (3) using a Beckman model DU spectrophotometer. A correction was made for the higher molecular weight material.

Pyrolysis

(*a*) *Vertical column method.*—The column of Pyrex glass tubing was 1 in. by 20 in. and jacketed to maintain temperatures between 100° C. and 300° C. Originally the column was filled with Berl saddles coated with the catalyst, sodium bisulphate, or *p*-toluenesulphonic acid. Later the latter catalyst was dissolved in the starting material. The system was maintained at 7 mm. and volatile products were collected in a dry-ice trap.

(*b*) *Batch method.*—The process was similar to that of Crowder and Elm (4). The system was maintained at a reduced pressure and the 250 ml. reaction flask was plunged into a Wood's metal bath at 280°–285° C. After seven to eight minutes the flask was removed from the bath and allowed to cool.

For molecular weight determinations the cryoscopic method of Gay (8) was used. Cyclohexane was purified by shaking with concentrated sulphuric acid and recrystallized four or five times to a freezing point depression constant of 21.3. Reagent grade naphthalene and a Beckmann thermometer were employed in determining the constant.

The ammonolysis investigations were carried out in an Aminco hydrogenator bomb. Nitrogen was determined by a micro-Kjeldahl method.

RESULTS AND DISCUSSION

The rate of oxidation of methyl erucate with peracetic acid prepared *in situ* and with varying concentrations of sulphuric acid as catalyst was readily followed by the method outlined and is shown in Fig. 1.

Rapeseed oil was hydroxylated with performic acid, then saponified and esterified with ethanol. The esters were then fractionally distilled. The mean molecular weight of each fraction was determined and included in Table I. The higher molecular weights indicated that some polymerization had occurred. The hydroxyl value of the polymeric residue was very low, about one-tenth of the theoretical value for the completely hydroxylated rapeseed oil triglycerides. Therefore, the molecular weight of the residual material was not accounted for by unsaponified hydroxylated erucin.

Through the intermediate of the reaction of peracetic acid on methyl and ethyl erucate the following compounds were synthesized: methyl 13,14-oxido-

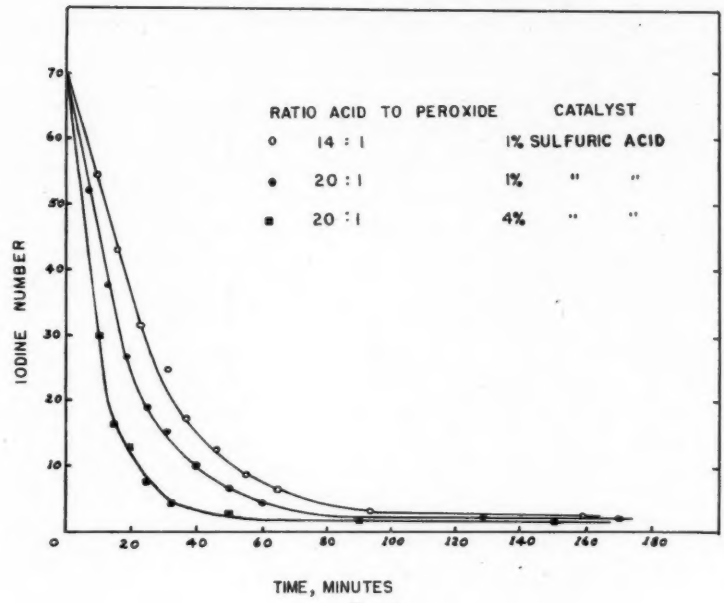

FIG. I

TABLE I

MOLECULAR WEIGHT DETERMINATIONS ON HIGH-VACUUM DISTILLATES AND RESIDUES FROM RAPESEED OIL HYDROXYLATION

Material	Fraction	Mean mol. wt.	Pressure, mm. Hg $\times 10^{-2}$	Temp. range, ° C.
Rapeseed oil after hydroxylation and methyl esterification	1*	92	48–50	150–155
	2	76	29	175–180
	3	361	27	210–215
	4	366	29	225–235
	Residue	1116		
Residue from a similar run only at lower vacuum	Residue after using lower vacuum	1263	1.5–2.0	230 Hydroxyl value 1.4% Theoret. hydroxyl value 14.2% based on iodine No. Sap. equiv. 281.

**The residue was about 40%. The main portions of the distillate were in fractions No. 3 and No. 4, 20–25% each.*

erucate, methyl and ethyl 13,14-diacetoxybehenate, methyl 13,14(14,13)-hydroxyacetoxybehenate, and ethyl 13,14-dihydroxybehenate. These were subjected to pyrolysis by both a continuous and batch method in the presence of a catalyst as outlined under Methods. The results are summarized in Table II.

TABLE II

PYROLYSIS OF HYDROXYLATED DERIVATIVES OF ERUCIC ESTERS

Starting material	Method*	Temp., °C.	Catalyst,** %	Product
Ethyl 13,14-dihydroxybehenate	*C*	205–210	***	Epoxy O 0.49% (11.7% oxido compds.) Carbonyl O 3.0% (71.7% ketones) Dienes 1.87%
	B	215–230	0.2	Largely ethyl 13-ketobehenate
Ethyl 13,14-diacetoxybehenate	*C*	290	0.2	Iodine No. 1.3 (theoret. 138.7 for complete conversion to diene)
	B	340–360	0.1	Iodine No. 60.3
Methyl 13,14-oxidoerucate	*B*	290–305	0.2	Epoxy O 0.28% (Starting material 4.04%) Iodine No. 17.6 Carbonyl O 2.03% (48% ketones)
Methyl 13,14-hydroxyacetoxybehenate	*B*	330–370	0.2	Conjugated diene 60.5% Carbonyl O 0.81% (19% ketones)

**B—batch pyrolysis.*
C—column pyrolysis.
***p-Toluenesulphonic acid.*
****Berl saddles coated with sodium bisulphate instead of p-toluenesulphonic acid.*

Pyrolysis of both dihydroxy and epoxy derivatives appeared to yield largely ketonic material with no significant amount of conjugated diene. The diacetoxy derivative yielded some diene while the hydroxyacetoxy derivative on pyrolysis yielded as much as 60% diene, the chief by-product was still the ketone. This is largely in agreement with the results of Crowder and Elm (4), except that they obtained some unsaturation on pyrolysis of the epoxy derivative. The batch method with *p*-toluenesulphonic acid as catalyst was found to give more favorable yields of desired products than the continuous method. This was probably due in part to the higher temperature of the batch process.

The attempt to produce 13,14(14,13)-hydroxyamino derivatives either by ammonolysis of oxido or bromohydrin derivatives was unsuccessful. Treatment of epoxide ethyl esters of rapeseed oil with concentrated aqueous ammonia at 60° C. for 24 hr. largely resulted in the production of the ammonium salt of the epoxy acids. Using liquid ammonia in a bomb at 75° C. for three and one-half hours and ammonium chloride as a possible catalyst resulted in recovery of largely unchanged starting material. More strenuous conditions at 165° for five and one-half hours yielded largely polymerized material. When benzene was used as an inert solvent at this higher temperature, only unchanged material was recovered. The use of a new derivative, oxidoerucamide, at the same temperatures also did not yield the desired product. Treatment of the bromohydrin of methyl erucate with liquid ammonia at 150° for six hours also yielded a polymer and a test for bromide.

Apparently the oxido derivative of the compounds investigated is relatively inert to ammonolysis under mild conditions, with liquid or aqueous ammonia. Under more severe reaction conditions with liquid ammonia the ring is evidently broken with the resultant loss in epoxy oxygen but polymerization follows without the production of the aminohydroxy derivative.

Oxidoerucamide was prepared by peracetic acid oxidation of erucamide, essentially according to the procedure of Roe *et al.* (16) for the epoxidation of oleamide. After several recrystallizations from ethanol a 65% yield of pure product was obtained, m.p. 101.5°. Analysis—N 3.90%, theoretical 3.96%; epoxy oxygen 4.50%, theoretical 4.53%. The product was also obtained by treatment of ethyl oxidoerucate with liquid ammonia.

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FREE RADICALS BY MASS SPECTROMETRY

III. RADICALS IN THE THERMAL DECOMPOSITION OF SOME BENZENE DERIVATIVES[1]

By K. U. Ingold[2] and F. P. Lossing[3]

ABSTRACT

The following benzene derivatives have been pyrolyzed in a free radical mass spectrometer: benzene, toluene, benzaldehyde, anisole, diphenyl, phenyl ether, and benzyl ether. The products and intermediates were analyzed, particular attention being paid to the formation (and stability) of any aromatic free radicals found. The phenyl, benzyl, phenoxy, and benzoyl radicals, as well as atomic carbon, were detected. The first two could be obtained abundantly and are fairly stable below 1150°. The oxygenated radicals were much less abundant and appeared to be less stable.

INTRODUCTION

The use of modified mass spectrometers for the detection and identification of free radicals formed by thermal dissociation has been described by various authors (3, 8, 14, 15, 19). However, the method has been applied only to light radicals such as methylene, methyl, and ethyl. It was thought to be of interest to try to extend the method to the study of heavier radicals such as phenyl and benzyl.

Evidence for the existence of the phenyl radical was first obtained in 1933 by Dull and Simons (2) from the thermal decomposition of tetraphenyl lead and the subsequent reaction of the phenyl radical with mercury. The radical has also been produced by the photochemical decomposition of tetraphenyl lead (13). In 1934 Horn and Polanyi (9) produced the phenyl radical by the diffusion flame method; it was detected by reaction with iodine. However, Paneth and Lautsch (17) who repeated this work did not detect any free radicals.

In view of the conflicting opinions about the phenyl radical, Glazebrook and Pearson (6) studied the radicals produced in the photolysis of aromatic ketones with the aid of tellurium mirrors. In the absence of tellurium, the photolysis of acetophenone gave some evidence for the presence of diphenyl, benzil, and dibenzoyl ethane. In the presence of tellurium, Ph_2Te, Me_2Te, and PhMeTe were identified, the ketone molecule having split into phenyl and methyl radicals which then reacted with the tellurium. The occurrence of benzil suggests the intermediate formation of the benzoyl radical (C_6H_5CO) which can dissociate to a phenyl radical and carbon monoxide. The photolysis of benzophenone also yields active fragments, and it can be argued by analogy that it undergoes simple fission like acetophenone.

The radical has also been detected in solution both by the decomposition

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of benzene diazonium chloride (28) and by the action of copper bronze on phenyl iodide (18).

In 1949 Schüler and Reinebeck (20) decomposed a number of benzene derivatives by electron impact into both excited and unexcited radicals. Both identical (i.e. radical) and characteristic emission spectra were observed. The phenyl radical was found in benzene and a number of monosubstituted benzenes, including toluene. The benzoyl radical was detected in acetophenone and benzophenone, and some evidence for the existence of radicals in benzaldehyde was obtained from the absorption spectra. No radicals were detected in anisole.

The benzyl radical ($C_6H_5CH_2$) was first prepared by Paneth and Lautsch (17) in 1935 by decomposing tetrabenzyl tin, dibenzyl ketone, and also by the reaction of benzyl chloride with sodium vapor. It has also been found in the thermal decomposition of toluene by mirror techniques (7) and by the formation of dibenzyl (24). The benzyl radical has also been produced in the decomposition of some substituted toluenes (1, 12, 16, 25, 27) and by the production of free radicals in the presence of toluene (26).

EXPERIMENTAL

A description of the free radical mass spectrometer used in this work has been given in previous papers (14, 15). The compound to be studied was carried, at a partial pressure of a few microns of mercury, through the tubular quartz reactor in a stream of helium at total pressures of a few millimeters. Since the compounds with two aromatic nuclei had very low vapor pressures, the mixture of helium and the compound was made by passing the helium through a trap containing the compound at a suitable temperature. Since the lines to the mass spectrometer were not heated, this temperature had to be below room temperature. Even by this method it was not possible to pick up enough benzophenone or benzil to permit the study of their decompositions, and the maximum partial pressure of benzyl ether which could be obtained was quite low. In order to reduce condensation of the reactants on the water-cooled wall of the reactor, it was necessary to preheat the cooling water above room temperature.

The detection of the radicals was made, using 50 volt electrons, by subtraction of the spectra of any compounds of higher molecular weight which were found to be present in significant amounts. To give greater precision, these spectra were obtained at temperatures just below the decomposition temperatures of the reactants. Attempts to detect phenyl and benzyl at low electron energies by the method of Eltenton (3) gave negative results. This was surprising and can only be explained by a very low ionization cross section for these radicals at the low electron energies required to eliminate the mass 77 and 91 peaks from the spectra of the parent compounds. In the absence of confirmation of the presence of the radicals by the low electron energy method, it was of great importance to ensure that peaks of mass 77 and 91 were due to ionized phenyl and benzyl and not produced by electron

impact from some substance of higher molecular weight. Fortunately, the dimeric forms such as diphenyl and dibenzyl were present only in trace amounts, and in the spectra of these the parent molecular ion is many times more abundant than the fragments at mass 77 and 91. It has been assumed that what remains of the parent radical peak after subtraction of the contributions from all known products of higher molecular weight can be attributed to the radical itself. It might be noted that in the most unfavorable cases the contribution to the radical peak from substances of higher molecular weight is never more than 90–95%. In more favorable cases, it may be as low as 50%. There still remains a rather remote possibility that at least a portion of these radical peaks could be due to some unsuspected molecular species in whose spectrum the 77 and 91 peaks are by far the most abundant, and for which the parent molecular ion is practically absent.

Material for Pyrolysis

The benzene used was Nichols Reagent Grade, the toluene was Phillips' Research Grade. The benzaldehyde, anisole, and diphenyl were supplied by the Matheson Co. The phenyl ether used was obtained from Dr. Theodor Schuchardt G.m.b.H. Gorlitz, and the benzyl ether was obtained from the Eastman Kodak Co.

RESULTS

The thermal decomposition of benzene, toluene, benzaldehyde, anisole, diphenyl, phenyl ether, and benzyl ether were studied. The phenyl, benzyl, phenoxy (C_6H_5O), and benzoyl radicals were identified in these decompositions, and in two cases methyl radicals were found. Without considerable modification of the present apparatus, it was found to be impossible to measure the sensitivity of the instrument to these radicals by the method used for methyl (15), owing to the large number of products formed, and to the difficulty of preventing the heavier products and reactants from condensing or adsorbing in the cooler parts of the reactor. In the absence of any such relationship, the sensitivities of the radicals were assumed to be all the same with 50 volt electrons and to be equal to two-thirds the sensitivity of benzene. This assumption is not likely to be in error by more than a factor of two, if one can use the case of methyl and methane as an analogy (15). For other materials whose sensitivities were not measured the same assumed sensitivity was used; in the tables the use of this value is indicated by an asterisk. For carbon, the sensitivity value is purely arbitrary, and the pressures given in the tables are useful only as a rough guide to the relative amounts of carbon formed at different temperatures.

Benzene

The products found in the pyrolysis of benzene at three temperatures are given in Table I. A fairly large proportion of the reaction appears to go directly to carbon and hydrogen. Only a trace of the phenyl radical was found. Of the other products, acetylene was the most abundant.

Toluene

Benzyl radicals were found in abundance in the pyrolysis of toluene, as

TABLE I

DECOMPOSITION PRODUCTS OF BENZENE (He PRESSURE = 7.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

Products	1350° C.	1400° C.	1450° C.
Hydrogen	2.68	3.62	4.96
Carbon*	0.05	0.10	0.23
Methane	0.01	0.03	0.06
Acetylene	0.09	0.06	0.01
Ethylene	0.01	0.02	0.03
Butadiyne	0.02	—	—
Phenyl*	—	0.01	0.01
Initial benzene	4.34	4.34	4.34
Remaining benzene	3.30	2.82	2.12

**Denotes use of assumed sensitivity as described in text.*

shown in Table II. Methyl and a trace of phenyl radicals were also present at the two lower temperatures. Acetylene and butadiyne were the most important hydrocarbon fragments. It should be noted that since tolyl radicals are isomeric with benzyl radicals, the possibility that the radicals of mass 91 are tolyl radicals cannot be ruled out.

TABLE II

DECOMPOSITION PRODUCTS OF TOLUENE (He PRESSURE = 7.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

Products	1150° C.	1225° C.	1300° C.
Hydrogen	1.77	4.40	8.02
Carbon*	0.04	0.08	0.15
Methyl	0.05	0.06	—
Methane	0.07	0.13	0.11
Acetylene	0.11	0.48	1.06
Ethylene	0.11	0.16	0.13
Ethane	0.01	0.03	0.03
Butadiyne	0.11	0.50	0.79
Phenyl*	0.01	0.01	—
Benzyl*	0.27	0.14	0.02
Benzene	0.16	0.26	0.25
Diphenyl*	Trace	Trace	Trace
Dibenzyl*	Trace	Trace	Trace
Initial toluene	2.5	2.5	2.5
Remaining toluene	1.6	0.8	0.19

**Denotes use of assumed sensitivity as described in text.*

Benzaldehyde

The major products from the decomposition of benzaldehyde at 1100° and 1400° C. were hydrogen, carbon monoxide, and benzene. Other products were carbon, methane, acetylene, ethylene, formaldehyde, butadiyne, and diphenyl. There is some evidence for the formation of acrolein and 1,5-hexadiyne-3-ene. Phenyl radicals and a trace of benzoyl radicals were detected.

Carbon monoxide was evolved from the furnace at high temperatures even

after the benzaldehyde flow had been stopped, indicating that some polymerization had also occured. This effect persisted after the experiments with benzaldehyde were completed, and at high temperatures interfered with the measurement of the 28 peak in the subsequent compounds (see note in Table V).

Anisole

Anisole was pyrolyzed at 800° and above; the products at 800° are listed in Table III. A trace of benzyl alcohol and diphenyl were also found. Phenyl and methyl radicals were abundant, the phenoxy radical was also present in small amounts.

TABLE III

DECOMPOSITION PRODUCTS OF ANISOLE (He PRESSURE = 2.8 MM.)
PARTIAL PRESSURES IN MICRONS Hg

Products	800° C.	Products	800° C.
Hydrogen	0.30	Phenyl*	0.05
Methyl	0.06	Phenoxy*	0.01
Methane	0.11	Phenol*	0.09
Ethylene	0.03	Benzene	0.28
Ethane	0.02	Toluene	0.03
Carbon monoxide	0.37		
Formaldehyde	0.04	Initial anisole*	0.61
Butadiyne	0.02	Remaining anisole*	0.24

**Denotes use of assumed sensitivity as described in text.*

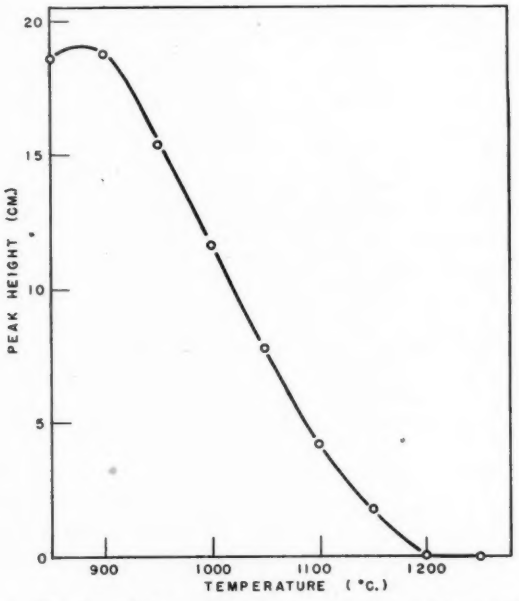

FIG. 1. The thermal decay of phenyl radicals produced from anisole.

The phenyl radical concentration decreased with increase of temperature (Fig. 1), being completely absent at 1200° and above.

Diphenyl

Diphenyl was decomposed from 1300° to 1500°C. At these high temperatures only a trace of phenyl was observable. Other products detected included hydrogen, carbon, acetylene, ethylene, butadiyne, and benzene.

Phenyl Ether

The major products of the decomposition of phenyl ether at four different temperatures are given in Table IV. Other products with the following masses were detected:

118, possibly vinylphenyl ether,
76, possibly 1,5-hexadiyne-3-ene,
66, possibly 1-hydroxybutadiyne.

Traces of the phenoxy radical and phenol were also detected.

TABLE IV

DECOMPOSITION PRODUCTS OF PHENYL ETHER (He PRESSURE = 8.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

Products	970° C.	1040° C.	1130° C.	1175° C.
Hydrogen	1.08	1.96	2.84	2.68
Carbon*	0.01	0.04	0.05	0.08
Methane	—	0.02	0.03	0.03
Acetylene	0.03	0.22	1.03	1.19
Ethylene	0.05	0.15	0.08	0.12
Carbon monoxide	0.44	1.24	1.28	1.39
Butadiyne	0.07	0.06	0.17	0.29
Phenyl*	0.03	0.10	0.08	0.07
Benzene	0.28	0.54	0.56	0.47
Diphenyl*	0.02	0.02	0.03	0.03
Initial $(C_6H_5)_2O$*	0.93	0.93	0.93	0.93
Remaining $(C_6H_5)_2O$*	0.42	0.11	0.03	0.02

**Denotes use of assumed sensitivity as described in text.*

Benzyl Ether

The decomposition products of benzyl ether at three different temperatures are given in Table V. In addition to the products listed some acetylene and benzyl alcohol were detected. There appeared to be little or no toluene present. Both benzoyl and phenyl radicals were present in small quantities, but free benzyl was abundant, being present in this compound in a larger ratio to the other products than in the decomposition of toluene. This is probably due to the fact that this compound can be decomposed at a much lower temperature where the benzyl radical is fairly stable. It should be noted that, at the highest temperature studied, viz. 1290° C., the amount of benzyl present shows a marked decrease.

TABLE V

DECOMPOSITION PRODUCTS OF BENZYL ETHER (He PRESSURE = 8.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

Products	860° C.	1050° C.	1290° C.
Hydrogen	0.10	0.25	0.54
Methane	—	0.01	0.02
Ethylene	0.01	0.03	0.02
Carbon monoxide	0.02	0.10	See note
Formaldehyde	—	0.02	0.04
Butadiyne	0.01	0.01	0.01
Phenyl*	0.005	0.005	0.004
Benzyl*	0.05	0.05	0.01
Benzene	0.01	0.03	0.03
Benzoyl*	0.004	0.01	0.002
Benzaldehyde*	0.03	0.03	—
Dibenzyl	Trace	Trace	Trace
Initial $(C_6H_5.CH_2)_2O$*	0.078	0.078	0.078
Remaining $(C_6H_5CH_2)_2O$*	0.05	0.03	0.004

Note: As previously described in the text, the carbon monoxide measurement was invalidated by the decomposition of benzaldehyde polymers.
**Denotes use of assumed sensitivity as described in text.*

DISCUSSION

Benzene

Although the photolysis (11, 29) and mercury photosensitized (4) decomposition of benzene have been fairly thoroughly investigated, there have been very few examinations of the uncatalyzed thermal decomposition, the only one of note being that of Hein and Mesée (7*b*) who, by the use of mercury vapor, were able to detect radicals. The results of their microanalysis gave no clue as to the nature of the organic residue, but they concluded that the mercuriated phenyl groups were partially hydrogenated by the hydrogen set free in the pyrolysis. The present investigation shows that while phenyl radicals are undoubtedly a product they are present in such small amounts that they cannot play any important part in the reaction. The only important process appears to be a direct decomposition to hydrogen and free carbon. Small amounts of butadiyne and some lower hydrocarbons are also formed. The trace of methane which was found is rather surprising; it might arise either by the direct action of hydrogen on the free carbon present in the reactor, or by the breakdown of various unsaturated primary products, being detected only because it is rather more stable than the majority of hydrocarbons.

Toluene

The pyrolysis of toluene has been rather more thoroughly investigated than that of benzene. Jost and Müffling (10) found that $Hg(CH_3)_2$ had no effect on the rate of decomposition at 690°, and therefore concluded that the reaction is not a chain process. By the use of mercury vapor, Hein and Mesée (7) isolated mercury dibenzyl from which they concluded that the first step in the decomposition of toluene is the rupture of one of the C–H

bonds in the methyl group. More recently Szwarc (24) has confirmed this result by the isolation of dibenzyl as a product of the reaction. The only other products reported by Szwarc are hydrogen, methane, and benzene; he suggests the following mechanism for the decomposition of toluene in the temperature range 738° to 864° C.

$$C_6H_5CH_3 \rightarrow C_6H_5.CH_2 + H \quad (1)$$

$$C_6H_5.CH_3 + H \rightarrow C_6H_5.CH_2 + H_2 \quad (2)$$

and

$$C_6H_5.CH_3 + H \rightarrow C_6H_6 + CH_3 \quad (3a)$$

$$C_6H_5.CH_3 + CH_3 \rightarrow CH_4 + C_6H_5.CH_2 \quad (3b)$$

or

$$C_6H_5.CH_3 + H \rightarrow C_6H_5 + CH_4 \quad (4a)$$

$$C_6H_5CH_3 + C_6H_5 \rightarrow C_6H_6 + C_6H_5.CH_2 \quad (4b)$$

$$2\ C_6H_5.CH_2 \rightarrow (C_6H_5.CH_2)_2 \quad (5)$$

Neither ethane nor diphenyl were found, either or both of which might have been expected from the dimerization of the radicals produced in reactions (3*a*) and (4*a*) respectively. In the present experiments which were carried out some 300° to 450° higher, small amounts of both methyl and phenyl radicals were detected, as well as their dimers. Only a trace of dibenzyl was detected at all temperatures, and the benzyl radical, though abundant at the lowest temperatures, was found to decrease markedly with rise of temperature, evidently being unstable above 1150°. A rough value of 68 ± 4 kcal. was obtained for the temperature coefficient of the disappearance of the benzyl radical. The presence of carbon and various unsaturated hydrocarbons, e.g. acetylene and butadiyne, in the products shows that at least some of the benzene nuclei are being broken at this temperature, so this temperature coefficient may correspond to breakdown of the benzyl radical. But, because of the relatively high degree of decomposition with which it is necessary to work in the present method, other alternative reactions which lead to disappearance of the radical, such as disproportionation or hydrogen abstraction from compounds other than toluene, will occur simultaneously. It is therefore not possible to assign this value to any one particular reaction.

The present results are in general agreement with those of Szwarc when it is remembered that they were done at temperatures several hundred degrees higher where some of the benzene nuclei are ruptured, but it also seems possible that at these high temperatures direct breakdown to a phenyl and a methyl radical occurs

$$C_6H_5.CH_3 \rightarrow C_6H_5 + CH_3\,. \quad (6)$$

Benzaldehyde

The thermal decomposition of gaseous benzaldehyde has been studied by Smith and Hinshelwood (21) in a static system. The chief products were benzene and carbon monoxide, but some diphenyl was also formed. The reaction was approximately first order and was partially inhibited by nitric oxide. From the results of their inhibition experiments Smith and Hinshelwood concluded that the mechanism of decomposition must involve two kinds of radical, one of which can only propagate the chain after itself decomposing

to give a smaller radical, and that the chains are broken by recombination of two different kinds of radical. Their proposed mechanism of decomposition is given below.

$$C_6H_5CHO \rightarrow C_6H_5 + CHO \quad (7)$$
$$CHO \rightarrow CO + H \quad (8)$$
$$H + C_6H_5CHO \rightarrow C_6H_6 + CHO \quad (9)$$
$$H + CHO \rightarrow H_2 + CO \quad (10)$$

However, Steacie (23) suggests that reaction (9) is unlikely compared with

$$H + C_6H_5CHO \rightarrow H_2 + C_6H_5CO, \quad (11)$$
$$C_6H_5CO \rightarrow C_6H_5 + CO\,. \quad (12)$$

Although the present experiments were done at a considerably higher temperature, they seem, nevertheless, to be in general agreement with the modified mechanism which replaces reaction (9) by reaction (11) and (12). The benzoyl radical is undoubtedly one of the products, but it is not nearly as plentiful as phenyl and must therefore be rather less stable. Once again at these high temperatures some of the benzene nuclei are broken down to carbon and various unsaturated hydrocarbons.

However, by analogy with toluene it is to be expected that the $C_6H_5C(O)-H$ bond will be much more readily broken than the C_6H_5–CHO bond, for the benzoyl radical will be resonance stabilized in the same manner as benzyl. The mechanism given by Smith and Hinshelwood was derived from a comparison with the mechanisms proposed for the decomposition of simple aliphatic aldehydes, e.g. acetaldehyde and propionaldehyde, but it seems doubtful that such mechanisms can be extended to include benzaldehyde. Another possible reaction scheme which covers the experimental data is therefore given.

$$C_6H_5CHO \rightarrow C_6H_5CO + H \quad (13)$$
$$C_6H_5CO \rightarrow C_6H_5 + CO \quad (12)$$
$$C_6H_5 + C_6H_5CHO \rightarrow C_6H_6 + C_6H_5CO \quad (14)$$
$$H + C_6H_5 \rightarrow C_6H_6 \quad (15)$$
$$C_6H_5 + C_6H_5CO \rightarrow C_6H_5COC_5H_5 \quad (16)$$

Reactions (11) and (15) will remove the H atoms formed in the primary step. Diphenyl will be formed by the dimerization of phenyl radicals.

It is quite probable that some of the reaction goes by a direct molecular rearrangement to benzene and carbon monoxide

$$C_6H_5CHO \rightarrow C_6H_6 + CO\,. \quad (17)$$

Anisole

The thermal decomposition of anisole from 482° to 707° C. was studied in a flow system by Freĭdlin *et al.* (5). They concluded that the reaction proceeds primarily to phenol with the probable formation of a free alkyl radical, and simultaneously undergoes rearrangement to benzyl alcohol. Some benzene and toluene were also found. In the present investigation methyl, phenyl, and phenoxy radicals were detected. These, by dimerization and hydrogen abstraction, give rise to ethane, methane, diphenyl, and some of the benzene

and phenol. Toluene comes from the recombination of methyl and phenyl radicals. Several primary steps appear possible.

$$C_6H_5OCH_3 \rightarrow C_6H_6 + CO + H_2 \quad (18)$$

$$C_6H_5OCH_3 \rightarrow C_6H_5 + CH_3O \quad (19)$$

$$C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3 \quad (20)$$

The methoxy radical was not detected and apparently decomposes at these temperatures to formaldehyde and a hydrogen atom. To account for the proportions of the products found would require that about half the phenoxy radicals formed react together, with one ring rupturing and the other forming a phenyl.

$$2\ C_6H_5O \rightarrow C_6H_5. + 2CO + C_4H_5 \quad (21)$$

The C_4H_5 could then give rise to carbon, hydrogen, ethylene, and butadiyne. Only a trace of benzyl alcohol was detected, so that at these temperatures it is either much less stable than anisole or, as is more probable, only a small part of the reaction goes by a "carbinol-type" rearrangement.

A plot of the peak height due to the phenyl radical as a function of the temperature is given in Fig. 1. From this curve a temperature coefficient of 39 ± 3 kcal. was obtained for the disappearance of the phenyl radical. It is difficult to assign this value to a given reaction since, over this temperature range, hydrogen abstraction (low E) and actual breakdown of the phenyl radical (high E) are probably in competition.

Diphenyl

The decomposition of diphenyl at high temperatures can be represented by:

$$C_6H_5.C_6H_5 \rightarrow 2C_6H_5 \rightarrow H_2 + C + C_2H_2 + C_2H_4 \text{ etc.}, \quad (22)$$

$$C_6H_5 + RH \rightarrow C_6H_6 + R. \quad (23)$$

Phenyl Ether

The decomposition of phenyl ether has previously been studied only at low temperatures (22) (440°–490° C.). In the present experiments the stoichiometric relationship above 1100° was found to be

$$C_6H_5.O.C_6H_5 \rightarrow CO + 2H_2 + C_2H_2 + \tfrac{1}{2}C_6H_6 + \text{unsaturated hydrocarbons and carbon.} \quad (24)$$

Below 1100° there is very much less acetylene.

The most important primary step is presumably breakdown to a phenyl and a phenoxy radical, but the presence of vinylphenyl ether in the products shows that one of the rings can break open before the C–O bond is broken. Diphenyl arises from the recombination of two phenyl radicals, and benzene and phenol are formed from phenyl and phenoxy respectively by hydrogen abstraction. At 970° the amount of carbon monoxide formed does not correspond to the amount of phenyl ether decomposed, and much of the oxygen must be present in other compounds such as 1-hydroxybutadiyne and vinylphenyl ether. Above 970° almost all the oxygen appears as carbon monoxide.

A temperature coefficient of 47 ± 3 kcal. was obtained for the disappearance of the phenyl radical. As explained for anisole this probably represents a compound value for decomposition and hydrogen abstraction. This value was

obtained at a higher temperature where more breakdown and less abstraction would be expected, so that a larger temperature coefficient is not altogether unexpected.

Benzyl Ether

The primary step in the decomposition of benzyl ether is presumably the breaking of a C–O bond:

$$(C_6H_5CH_2)_2O \rightarrow C_6H_5CH_2 + C_6H_5CH_2O\,. \qquad (25)$$

The $C_6H_5CH_2O$ radical can undergo a number of different reactions, some of which are listed below.

$$C_6H_5CH_2O \rightarrow C_6H_5 + H.CHO \qquad (26)$$
$$C_6H_5CH_2O \rightarrow C_6H_6 + CO + H \qquad (27)$$
$$C_6H_5CH_2O \rightarrow C_6H_5CO + H_2 \qquad (28)$$
$$C_6H_5CH_2O \rightarrow C_6H_5CHO + H \qquad (29)$$

All the products shown (except H atoms) were found. The benzoyl radical might also give benzaldehyde by hydrogen abstraction, or alternatively benzaldehyde might give the radical by loss of a hydrogen atom.

The virtual absence of toluene in the products proves that the direct molecular rearrangement to toluene and benzaldehyde does not occur.

$$(C_6H_5CH_2)_2O \rightarrow C_6H_5CH_3 + C_6H_5CHO \qquad (30)$$

Moreover, it means that the benzyl radical does not readily abstract hydrogen atoms.

To sum up the analytical data given in this paper, it may be noted that hydrogen, carbon, and unsaturated hydrocarbons form a larger proportion of the products as the temperature is increased, and in those compounds which have to be cracked at high temperatures. The phenyl and benzyl radicals can be obtained copiously below about 1150° C.; the best sources were found to be anisole and benzyl ether respectively. The phenoxy and benzoyl radicals appear to be less stable and could not be obtained in large amounts from any of the compounds studied.

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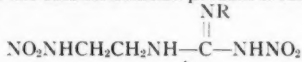
THE ULTRAVIOLET ABSORPTION SPECTRA OF NITROGUANIDINE DERIVATIVES[1]

By A. F. McKay and C. Sandorfy[2]

ABSTRACT

The ultraviolet absorption spectra of the ammonia and amine addition products of 1-nitro-2-nitramino-2-imidazoline verify the linear structure *A* for these compounds. Also the ethanol addition product is considered on the basis of

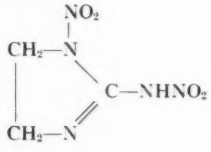


A

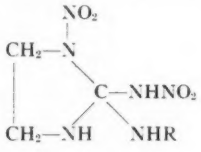
its absorption spectrum to be N-β-nitraminoethyl-N-nitro-*o*-ethylisourea. The relative effects of the nitramino and nitroguanidine chromophores on the absorption spectra of several nitroguanidine derivatives are discussed.

INTRODUCTION

In 1948 the reaction of 1-nitro-2-nitramino-2-imidazoline with amines was described (6). It was found that one mole equivalent of ammonia, or amines, combined with 1-nitro-2-nitramino-2-imidazoline (I) to give addition products. These addition products were assigned a cyclic structure (II). The only evi-



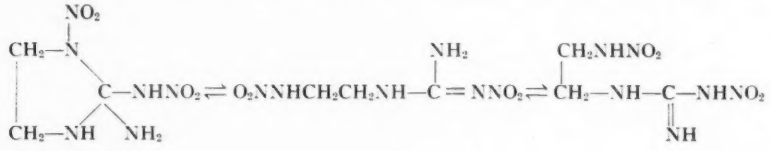
I



II

R = H or alkyl

dence for this structure was that the ammonia addition product gave a low yield (26%) of 1,3-dinitro-2-imidazolidone, on nitration. Later titration data (1) indicated that the ammonia addition product was a monobasic acid which acquired a second acidic function on standing in alkali for 90 hr. On this basis the ammonium addition compound of 1-nitro-2-nitramino-2-imidazoline was represented as an equilibria mixture (III–V) which was considered to be predominantly displaced towards III. Since the ammonia addition



III IV V

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[2] *National Research Council of Canada Postdoctorate Fellow.*

product of 1-nitro-4-methyl-2-nitramino-2-imidazoline behaved as a bifunctional acid on titration it was assigned a linear structure VI. Finally,

$$NO_2NHCH_2CH(CH_3)NHC(=NH)—NHNO_2$$

VI

potentiometric titration of the *n*-propylamine addition product indicated it possessed one acidic group and it was assigned (2) the cyclic structure, 1-nitro-2-nitramino-2-*n*-propylaminoimidazolidine (II, R = $n - C_3H_7$). More recently (5) it has been shown that both the ammonia addition products of 1-nitro-2-nitramino-2-imidazoline and 1-nitro-4-methyl-2-nitramino-2-imidazoline possess almost identical ultraviolet absorption spectra. Moreover, on the basis of these absorption spectra linear structures V and VI respectively were assigned to these addition products. Now the ultraviolet absorption spectra of several compounds of this series have been determined and the results agree with linear structures for these adducts.

RESULTS AND DISCUSSION

All of the compounds having a nitroguanidine group displayed two absorption maxima at 205 mμ and 269–271 mμ (cf. Table I and Reference 5). Compounds possessing a primary nitramino group exhibit a maximum at 227–235 mμ (4) with a second increase in absorption beginning at 210 mμ (cf. Curve *A*, Fig. 1). The absorption spectrum of 1-nitro-2-nitramino-2-imidazoline is mainly of the nitroguanidine type (compare Curves *A* and *B* of Fig. 2). The effect of replacing the hydrogen at position 1 by a nitro group has been to double the E_{max} of the absorption maximum at 206 mμ. There has also been an increase in the molar extinction coefficient of the minimum.

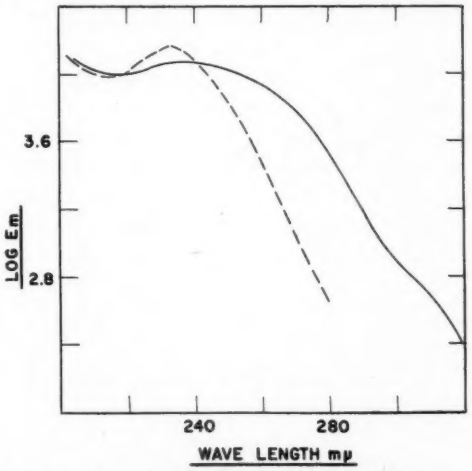


FIG. 1. Curve *A* – – – 1,3-Dinitraminopropane (water).
Curve *B* —— N-β-Nitraminoethyl-N′-nitrourea (water).

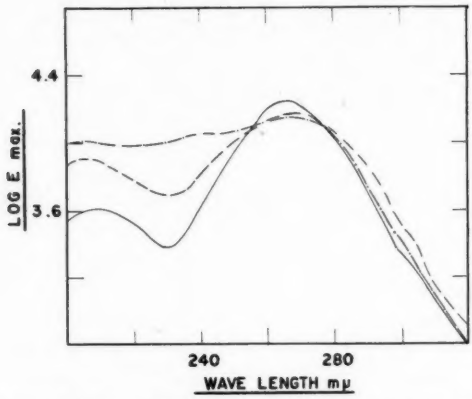


FIG. 2. Curve *A* —— 2-Nitramino-4(or 5)-methyl-2-imidazoline (water).
Curve *B* – – – 1-Nitro-2-nitramino-2-imidazoline (water).
Curve *C* – · – N-β-Nitraminoethyl-N′-methyl-N″-nitroguanidine (water).

TABLE I

2-NITRAMINO-2-IMIDAZOLINES

Compound	Solvent	Absorption maxima			
		λ, mμ	log E_{max}	λ, mμ	log E_{max}
1-β-Hydroxyethyl-2-nitramino-2-imidazoline	Water	204	3.66	269	4.26
1-Methyl-2-nitramino-2-imidazoline	Water	208	3.60	268	4.17
2-Nitramino-4(or 5)-methyl-2-imidazoline	Water	209	3.62	265	4.25
1-Nitro-2-nitramino-2-imidazoline	Water	206	3.91	268	4.17

The ammonia and amino addition compounds of 1-nitro-2-nitramino-2-imidazoline (cf. Table II) have three absorption maxima at 205, 223–240, and 269–271 mμ. The ultraviolet absorption spectra of these compounds are a composite of the absorption spectra of the nitramino (VII) and nitroguanidino chromophores (VIII). Therefore 1-nitro-2-nitramino-2-imidazoline must add ammonia or amines with simultaneous opening of the ring to give compounds

$-NHNO_2$ VII

$N=C(-NH)-NHNO_2$ VIII

of structure IX. The two chromophores, viz. nitramino and nitroguanidino

$NO_2NHCH_2CH_2NH-C(=NR)-NHNO_2$ IX

R = H, CH_3, C_2H_5.

groups, are insulated by two saturated carbons and their effect would be expected to be additive, which it is. On the other hand, if amino and ammonia addition products of 1-nitro-2-nitramino-2-imidazoline possess the proposed (1, 2, 6) cyclic structures, carbon 2 would be saturated and the spectra ought to be purely of the nitramine type.

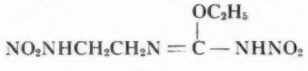
TABLE II

ABSORPTION SPECTRA OF LINEAR SUBSTITUTED NITROGUANIDINES

Compound	Absorption maxima					
	λ, mμ	log E_{max}	λ, mμ	log E_{max}	λ, mμ	log E_{max}
N-β-Nitraminoethyl-N′-nitroguanidine*			232	4.13	271	4.30
N-β-Nitramino-α-methylethyl-N′-nitroguanidine*			232	4.08	271	4.26
N-β-Nitraminoethyl-N′-methyl-N″-nitroguanidine**	205	4.02	240	4.05	269	4.17
N-β-Nitraminoethyl-N′-ethyl-N″-nitroguanidine**	205	4.04	239	4.05	269	4.16
N-β-Nitraminoethyl-N′-phenyl-N″-nitroguanidine**			223	4.13	271	4.20

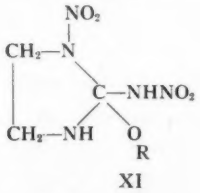
Solvent, alcohol. Measurements taken from Reference 5.
**Solvent, water.*

The height of the 230–240 mμ band depends on the overlap of this band with the strong neighboring band at 268 mμ. If the nitroguanidino band is shifted towards longer wave lengths, the overlap decreases rapidly and a minimum appears at the position of the former maximum. However, this minimum has a surprisingly high E value (ca. 7000) which corresponds fairly well to the absorption of one nitramino group. Then this band coalesces with the 205 mμ band to give a broad apparent band at about 220 mμ. This effect is observed in the spectrum of N-β-nitraminoethyl-N′-phenyl-N″-nitroguanidine (Curve *A*, Fig. 3). A similar effect is apparent in the spectrum of N-β-nitraminoethyl-N′-nitro-*o*-ethylisourea (X) (Curve *B*, Fig. 3).



X

For the latter compound X the following structure (XI, R = C_2H_5)



XI

was previously (6) suggested. Also the *n*-propyl alcohol addition product of 1-nitro-2-nitramino-2-imidazoline was assigned (3) this structure (XI, R =

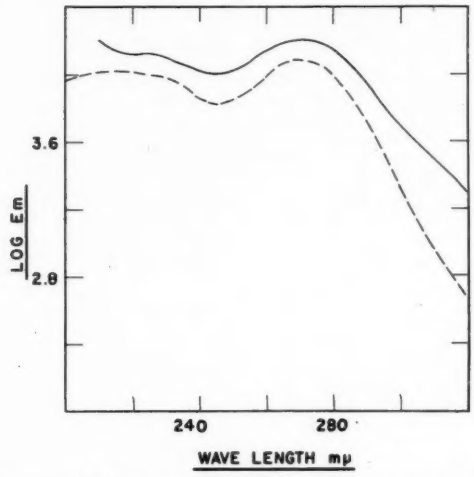


FIG. 3. Curve *A* —— N-β-Nitraminoethyl-N′-phenyl-N″-nitroguanidine (water).
Curve *B* – – – N-β-Nitraminoethyl-N′-nitro-*o*-ethylisourea (water).

nC$_3$H$_7$) on the basis of potentiometric titration data. However, this cyclic structure seems to be invalidated by the ultraviolet absorption spectra. In the cyclic structure, the two nitramino groups are insulated from each other by a tetrahedral carbon atom and the spectrum should be a pure nitramine spectrum with no 269 mμ band. Since a strong band is present at 271 mμ, it testifies to the existence in this compound (ethanol addition product of 1-nitro-2-nitramino-2-imidazoline) of the chromophore

$$HN=\underset{\displaystyle Y}{\overset{|}{C}}-NHNO_2$$

which is to be considered as a unique system of mobile electrons. One may consider the spectra of the compounds in Table I as due to this chromophore.

At 205–209 mμ both the nitramino and nitroguanidino groups absorb but the greater part of the absorption is due to the nitramino group as indicated by the extinction of the pure nitroguanidines.

The spectrum of N-β-nitraminoethyl-N′-nitrourea is closer to the nitramine type except for the unusual width of the 236 mμ band. This spectrum (Curve *B*, Fig. 1) indicates clearly that a band due to the chromophore

$$-NH-\overset{\displaystyle O}{\overset{\|}{C}}-NHNO_2$$

is hidden under the long wave length wing of the 236 mμ band. Its approximate position would be between 260 to 280 mμ.

EXPERIMENTAL

The spectra were measured on a Cary ultraviolet spectrophotometer. The compounds were analytically pure samples.

ACKNOWLEDGMENT

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THE FISSION YIELD OF Te^{134}[1]

By L. Yaffe,[2] Alison E. Day,[3] and Betsy A. Greer[4]

ABSTRACT

The fission yield of Te^{134} has been found to be 6.48% ± 0.47%. This makes the cumulative yield of I^{134} 7.71% using Glendenin's value of 0.19 as the independent fractional chain yield of I^{134}. This value, since it is very close to that found by Thode for Xe^{134}, offers additional confirmation of the 54 min. iodine assignment to mass 134.

INTRODUCTION

The fission yield concept was first introduced by Anderson, Fermi, and Grosse (1). It may be defined as the probability of a given nuclide being formed in fission. Owing to the work of many in the Plutonium Project (19) and others, the shape of the fission yield – mass curve is now well-known. For thermal neutron fission the curve is double-humped, showing that asymmetric fission is much more probable (600:1) than symmetric.

The data from which this curve is obtained are radiochemical and the errors which may be involved are usually quite large. In general, relative measurements may have an error of ± 5% and absolute measurements are probably no better than ± 10%. Thode and his collaborators have refined these measurements by use of the mass spectrometer where the precision is very great.

They determined (13) the yields of some of the Kr and Xe isotopes formed in fission and found that the yields of Xe^{133} and Xe^{134} were too high above the smooth mass–yield curve to be explained by experimental error. The yields determined by Thode were the cumulative yields for the chain. For example, a certain mass chain may consist of the following members, *A*, *B*, *C*, and *D*:

$$A \xrightarrow{\beta^-} B \xrightarrow{\beta^-} C \xrightarrow{\beta^-} D \text{ (stable)}.$$

B, for example, may be formed directly at the moment of fission or may be formed by the decay of its precursor *A*. Similarly for *C* and *D*, although the probability of the nuclide being formed as a primary fission fragment decreases as the stable end member is approached.

The yield of the nuclide formed directly as a fission fragment at the moment of fission is usually known as the *independent* yield, while that due to independent yield formation plus decay from its precursors is called the *cumulative* yield. The cumulative yield is most accurately determined by a mass spectrographic determination of the stable end member of the chain.

Glendenin (3, 5) has invoked the Mayer (14) nuclear shell hypothesis in an attempt to explain the high yields found by Thode for the 134 chain. He suggested that if a primary fission product is formed with one neutron, for example,

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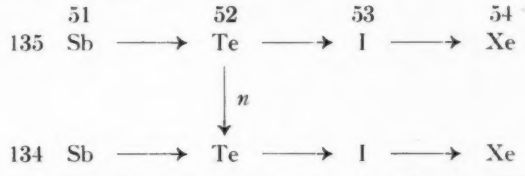
greater than that which composes a stable nuclear shell, the nucleus might de-excite by neutron emission of the last loosely-bound neutron, rather than by normal negaton decay.

In the case of the 134 and 135 chains,



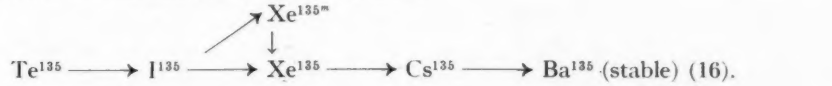
$_{52}Te^{135}$ has 83 neutrons in its nucleus, one more than the stable 82 shell, and the nuclear de-excitation may take place by neutron emission to the 134 chain. Such a mechanism would set up perturbations which would distort the smooth curve and produce anomalies. Recently (17) this suggestion has been extended to include primary fission fragments with one, three, five, and seven neutrons greater than that found in the stable shell, since these neutrons are all rather loosely bound.

Recently other anomalies have been found. Glendenin *et al.* (8) have found that mass 100 has a yield higher than that suggested by the smooth mass–yield curve. They follow the suggestion made by Thode (20) and others (15) that a stable shell may be a preferred mode of fission and suggest that the mass 100 particle is the complementary fragment of the mass 134 particle which is formed by a preferred mode of fission (e.g., $_{52}Te^{134}$ — 82 neutrons) in high yield.

When these anomalies began showing up it seemed advisable to re-investigate the yield of the earlier members of the 134 chain. The yield of I^{134} had been investigated previously by Katcoff *et al.* (11) and Yaffe and Mackintosh (23) who obtained yields of 5.7%. Glendenin (4) suggested that these results might be low because of poor exchange between the radioactive iodine atoms and the inert iodine carrier atoms used as a diluent. Such exchange difficulties had previously been noted by Glendenin *et al.* (7).

The independent yield of I^{134}, i.e., the amount formed directly in fission as distinct from that by Te^{134} decay, had been found by Glendenin (5). He calculated the activity expected from I^{134} decaying from Te^{134} after a known irradiation period. He then measured the I^{134} extracted at a certain time, the difference being due to the I^{134} formed in an independent manner. From this, the independent yield relative to some reference (5.6% for I^{135} in this case) may be calculated. He obtained an independent yield of 1.0% representing the fraction $0.19 \pm .03$ of the total chain yield. This figure will have to be revised slightly for the following reasons:

(1) I^{135} is a member of the following chain:



(2) Mass spectrographic evidence (20) gives the yield of Cs^{135} as 6.75% (using the fission yield of I^{131}, 3.14%, as a reference).

(3) The independent yield of Cs^{135} must be very small, (*a*) on the basis of any of the charge distribution in fission theories and (*b*) because the independent fission yield of its precursor Xe^{135} has been shown (2, 10) to be small (2.7% of the chain yield).

(4) By difference one gets the fission yield of I^{135} to be 6.57%, in good agreement with the results obtained by Pappas (18) i.e., 6.2%, which is higher than the value of 5.6% used by Glendenin.

(5) Glendenin used a yield of 5.0% for Te^{134} in his determination. The present work as well as data obtained from nuclear closed-shell effects in fission suggest a higher value. However, this operated only as a small correction factor and in the opposite direction to the other correction.

For the purposes of this paper the value obtained by Glendenin has been used.

Let us consider the formation of the various fission products which occur in the 134 chain during the fission process, and between the end of the irradiation and the separation of the I^{134} (which is to be measured) from the Te^{134},

$$134 \quad Sb \xrightarrow[< 10 \text{ min.}]{} Te \xrightarrow[44 \text{ min.}]{} I \xrightarrow[52.5 \text{ min.}]{} Xe \text{ (stable) (16).}$$

Let N = number of fissions per sec.,

Y_{Te} = fission yield of Te,

Y_i = independent fission yield of I,

X_1 and X_2 = number of atoms of Te^{134} and I^{134} respectively at any time t during irradiation,

T = time of irradiation,

λ_1 and λ_2 = disintegration constants of Te^{134} and I^{134} respectively.

During irradiation. —

$$\frac{dX_1}{dt} = Y_{Te}N - X_1\lambda_1$$

[1] and $$X_1 = \frac{Y_{Te}N}{\lambda_1}(1 - e^{-\lambda_1 T}),$$

$$\frac{dX_2}{dt} = X_1\lambda_1 + Y_iN - X_2\lambda_2$$

[2] so that $$X_2 = \frac{N(Y_{Te} + Y_i)}{\lambda_2}(1 - e^{-\lambda_2 T}) - \frac{Y_{Te}N}{\lambda_2 - \lambda_1}(e^{-\lambda_1 T} - e^{-\lambda_2 T})$$

after substituting from equation [1].

Between the end of irradiation and separation of I from Te. — Let the number of Te atoms at any time t, measured from the end of the irradiation, $= X_1' = X_1e^{-\lambda_1 t_1}$. Similarly the number of I atoms $= X_2' = X_2e^{-\lambda_2 t_1}$ + growth of I from Te since the end of irradiation.

Growth of I after irradiation. —

$$\frac{dX_2'}{dt} = X_1\lambda_1e^{-\lambda_1 t_1} - X_2'\lambda_2,$$

$$X_2' = \frac{\lambda_1}{\lambda_2 - \lambda_1} X_1(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}),$$

$$\text{total } X_2' = X_2 e^{-\lambda_2 t_1} + \frac{\lambda_1}{\lambda_2 - \lambda_1} X_1(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}),$$

and substituting from equations [1] and [2] gives

$$X_2'\lambda_2 = NY_i(1-e^{-\lambda_1 T})(e^{-\lambda_2 t_1}) + NY_{Te}\left\{\left[\frac{\lambda_2}{\lambda_1 - \lambda_2} e^{-\lambda_1 T} - \frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_2 T} + 1\right] e^{-\lambda_2 t_1}\right.$$

[3] $$\left. + \frac{\lambda_2}{\lambda_2 - \lambda_1}(1 - e^{-\lambda_1 T})(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1})\right\}$$

which is equal to the measured disintegration rate of I^{134} at time t_1, measured from the end of the irradiation.

If $T \gg 1/\lambda_1$ and $T \gg 1/\lambda_2$, then equation [3] simplifies to:

[4] $$X_2'\lambda_1 = N\left\{(Y_i + Y_{Te})e^{-\lambda_2 t_1} + Y_{Te}\frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1})\right\}.$$

The above treatment assumes that the measured disintegration constant is equal to the "effective" decay constant within the pile for both I^{134} and Te^{134}. This means that their capture cross sections are taken to be small.

If N, the fission rate, is known or measured, the above equation is soluble. However, a reference of known fission yield can be irradiated simultaneously and treated in the same manner. For this purpose we have used Ba^{139} (fission yield — 6.3%) which occurs in the following mass chain (16):

$$^{139}\text{Xe} \xrightarrow[41\text{ sec.}]{} \text{Cs} \xrightarrow[9.7\text{ min.}]{} \text{Ba} \xrightarrow[85\text{ min.}]{} \text{La (stable)}.$$

If the disintegration rates of the two are compared, the fission rate cancels out and Y_{Te} is then found in terms of the Ba^{139} yield. We here assumed its independent yield to be negligibly small compared to that of its precursor, Cs^{139}. This will be true on any reasonable charge distribution in fission theory.

EXPERIMENTAL

(*a*) *Irradiation*

Accurately weighed samples of uranyl nitrate hexahydrate (10 – 20 mgm.) were irradiated in various positions in the Chalk River NRX nuclear reactor for known lengths of time. The neutron spectrum in these positions was predominantly thermal. Two samples of uranyl nitrate were used in each irradiation, one for the Ba^{139}, the other for the I^{134} determination. The salt was enclosed in small sealed quartz ampoules. Irradiation times varied from 1 hr. to 16 hr.

(*b*) *Chemical Separation*

(i) *Iodine*

The silica tube was crushed in a beaker containing 2 *M* sodium carbonate to which a weighed amount of potassium iodide had been added as a carrier. A few milliliters of 5% sodium hypochlorite solution was added and the solution heated for at least five minutes to ensure completion of reaction (I^- to $I^{+7}O_4$). The solution was then transferred to a separating funnel containing enough

nitric acid to render the solution acid, the iodate reduced to iodine with hydroxylamine hydrochloride, and extracted into carbon tetrachloride. The iodine was further reduced (I_2 to I^-) using sulphurous acid, and the organic layer discarded. The iodide was then reoxidized with a sodium nitrite – nitric acid mixture and extracted with carbon tetrachloride. The sodium nitrite oxidation and sulphurous acid reduction cycle was repeated twice.*

The reduced solution was finally acidified with 6 *N* nitric acid. In some cases the solution was then placed on a weighed counting tray which contained excess silver nitrate. The tray was then heated under an infrared lamp and the dried silver iodide was weighed and the activity measured. In other cases the reduced solution was made up to a standard volume, an aliquot taken and treated in the above manner to obtain an activity measurement. This produced essentially a "weightless" source. The iodide content of the stock solution was determined gravimetrically, again precipitating silver iodide.

(ii) *Barium*

The barium was separated by a method described previously (9). This consisted of separation of the barium from the uranium and other fission products by several chloride, chromate, and nitrate separations with appropriate hold-back carriers added. In some cases the barium was precipitated finally as the sulphate, slurried with acetone, and transferred to a weighed counting tray. The weight of the barium sulphate whose activity was measured was then obtained. In experiments where the specific activity was very high, the final barium nitrate precipitate was dissolved in water and made up to a standard volume. An aliquot was then taken and dried on a counting tray. This produced essentially a weightless source.

The barium content of the stock solution was then obtained gravimetrically by a barium sulphate precipitation.

(*c*) *Measurements*

All activity measurements were made using "end-window" Geiger counters with window thicknesses of about 3 mgm. per cm.^{2} Where relevant, the following correction factors were made.

(i) *Self-absorption*

In some cases when the samples were not weightless, self-absorption curves were obtained (21). This correction was applied only in Experiments 1 – 9 inclusive.

(ii) *External Absorption*

Absorption of the β rays in the counter window and air gap between sample and counter window was corrected for in the following manner. Decay curves were obtained through various thicknesses of aluminum and absorption curves obtained from these. A slight extrapolation back to "zero absorption" was made to correct for any loss due to absorption.

(iii) *Back-scattering Corrections*

In cases of measurement of actual samples, conditions were such that

* *This method is almost identical with that used by Glendenin and Metcalf (6) and was the only method of many tried which gave complete exchange between active atoms and added inactive carrier atoms. These methods included addition of iodine in any or all of its many valence states and oxidation and reduction by various reagents.*

"saturation back-scattering" (22) was obtained in all cases. Corrections were made by measuring certain samples in identical "geometry" with no sample backing at all and then with "saturation" backing.

(iv) *Coincidence Losses*

A quench unit with a delay time of 600 μsec. was present in the circuit at all times and appropriate corrections were made where relevant.

(v) *Radioactive Decay*

Decay curves were obtained from measurements extending over at least 24 hr. The required activity (52.5 min. for I^{134} and 85 min. for Ba^{139}) was obtained from the background due to other active isotopes by the usual "peeling-off" technique. The straight line obtained from the semilogarithmic plot was extrapolated back to zero time which is defined as the removal of the desired element from its precursors (the first carbon tetrachloride extraction in the case of the iodine, and the first chloride precipitation in the case of the barium).

(vi) *Chemical Recovery*

For low specific activities the material which was to be measured directly on the counting tray was weighed. For high specific activities a small aliquot was placed on the counting tray and a chemical analysis performed on the remainder. The yield was then obtained by comparison with the amount of inactive carrier initially used.

RESULTS

The results are listed in Table I.

TABLE I

Expt. No.	Irrad'n. pos'n.	Time of irrad'n., T (hr.)	t_1. Time in minutes between end of irrad'n. and sep'n.		Corrected counts/min./mgm. $UO_2(NO_3)_2.6H_2O$ at zero time		Fission yield, %
			I^{134}	Ba^{139}	I^{134}	Ba^{139}	
1	Thermal column	16.00	40.0	36.2	93.1	72.2	6.70
2	"	9.00	81.5	98.5	39.4	27.9	6.05
3	"	16.33	59.0	46.0	102.1	86.4	6.46
4	"	16.05	46.8	51.3	68.8	55.0	6.04
5	"	15.65	62.5	45.0	76.1	65.3	6.61
6	"	10.34	31.2	45.2	80.7	58.0	6.42
7	"	16.55	29.3	41.3	93.7	72.5	6.07
8	"	15.94	32.3	35.2	115.7	85.2	6.80
9	"	16.75	39.7	57.8	100.9	64.5	6.87
10	Self-serve	8.00	104.0	84.2	2.26×10^6	1.66×10^6	6.85
11	"	8.05	57.3	59.0	2.76×10^6	2.22×10^6	6.08
12	"	8.00	85.0	86.1	3.91×10^6	3.04×10^6	6.27
13	"	5.00	77.7	87.5	5.08×10^6	3.50×10^6	6.58
14	"	5.00	72.8	71.2	2.24×10^6	2.22×10^6	5.76
15	"	5.00	54.3	54.0	4.73×10^6	4.24×10^6	5.56
16	"	5.00	79.3	84.5	4.88×10^6	3.38×10^6	6.81
17	"	5.00	41.0	40.7	3.31×10^6	2.88×10^6	5.81
18	"	5.00	63.2	67.3	7.98×10^6	5.39×10^6	7.08
19	"	5.00	52.8	42.5	8.01×10^6	6.34×10^6	6.81
20	"	1.00	63.7	63.7	3.36×10^6	2.66×10^6	6.64
21	"	1.00	63.2	84.0	2.23×10^6	1.53×10^6	6.61
22	"	1.00	80.7	107.3	1.84×10^6	1.08×10^6	7.60
						Average:	6.48 ± 0.47

DISCUSSION

The fission yield of Te^{134} was found to be 6.48% ± 0.47% using Glendenin's (5) value of 0.19 as the independent fractional yield of I^{134}. This gives a value for the cumulative yield of I^{134} of 7.71%. This agrees well with recent work by Pappas (18) who got values of 7.0% and 7.9% respectively.

No real genetic proof exists for the mass assignment of 134 for the 44 min. tellurium and the 52.5 min. iodine. The assignment is still on a tentative basis, although recent work by Katcoff, Miskel, and Stanley (12) on the range of fission fragments makes the assignment a highly probable one. The other possibility is mass 132. Thode *et al.* (13) found values of 4.6% and 8.2% respectively for the cumulative yields of the 132 and 134 chains (normalized to 3.1% for mass chain 131). Since the yield of the 54 min. iodine is much higher than the yield of the 132 chain and very close to that of the 134, this is considered additional evidence for the mass assignment.

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THE KINETICS OF COAGULATION OF AN EMULSION[1]

By G. Brady, L. Mandelcorn, and C. A. Winkler

ABSTRACT

Under suitable conditions, the coagulation of GR-S latex by sulphuric acid has been found to exhibit second order rate characteristics, and to be represented by the equation,

$$C = \frac{C_0}{1 + k\,(H^+)'\,C_0 t}$$

where C is the concentration of polymer at time t, C_0 is the initial concentration of polymer, and $(H^+)'$ is the concentration of H^+ ion in excess of the critical concentration necessary to initiate coagulation. Coagulation is accompanied by desorption of soap from the surface of the latex particles, and the variation of surface tension resulting from this follows the equation $\log \gamma = A - B \log t$, where γ is the surface tension and A and B are constants. Appropriate adjustment of the temperature was found to stabilize the emulsion markedly in the presence of acid. A mechanism for the coagulation process is considered.

The phenomenon of coagulation of colloidal systems is analogous in many respects to a chemical reaction, proceeding at a definite rate dependent on temperature and concentration. Frequently, however, it is a diffusion-controlled process to which the standard kinetic methods based on equilibrium between reactants, activated complex, and products cannot be applied. It is only when the probability of coalescence of the particles taking part in a collision is reduced, that is when the particles are relatively stable, that an equilibrium state can be postulated.

Statistical treatment of the problem by Smoluchowski and others (1, 6, 15, 16) has yielded the relation

[1] $$n = \frac{n_0}{1 + k\,\epsilon\,n_0 t}$$

to represent the number of particles n present at time t in a monodisperse system which at time $t = 0$ consists of n_0 primary particles. In this expression, ϵ is a numerical constant of value $0 \leqslant \epsilon \leqslant 1$, which depends on the charge or other stabilizing factors of the particle, and k is equal to $4\pi DR$, where D is the diffusion coefficient of the primary particle and R is the radius of its sphere of attraction. R is defined as the distance to which two particles must approach for coalescence, which must be equal to at least twice the radius of the primary particles. This equation has been found to be generally valid when $\epsilon \simeq 1$ (9, 19, 21), that is, for uncharged particles, but has been found to be in poor agreement with experiment in many cases where the charge on the particles has been only partially neutralized (slow coagulation) (3, 4, 7).

With emulsions the particles are generally stabilized by emulsifiers adsorbed at the interface between the internal phase and the external suspending

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medium. Coagulation of emulsions results when this film is removed or weakened sufficiently to decrease the stability of the particles to a value below the critical threshold potential. The process is more complicated than with particles which are simply charged, in that the rate of removal of the adsorbed film may be a rate-controlling factor. Also, observations by Lewis (10) and Powis (13) indicate that the primary process in emulsion coagulation may be an adherence of the particles in which their physical identity in the resulting aggregate is retained. This may be followed by coalescence of these particles into a single mass, or by disintegration of the aggregates before coalescence is achieved. Thus it is probable that the simple mechanism postulated by von Smoluchowski may not apply rigorously to this type of system.

In this paper are presented results for coagulation of GR-S latex, type II, with sulphuric acid. Experiments were made to determine the rate of coagulation and its dependence on the concentrations of latex and acid, and on temperature. Efforts were also made to determine the rate of desorption of soap during the coagulation and to seek a correlation between this phenomenon and the rate of coagulation.

EXPERIMENTAL AND RESULTS

Determination of Rate of Coagulation

The rate of coagulation was determined by centrifuging the coagulated material from the system. By adjusting the speed and time of centrifuging, particles of any desired size could be separated from the emulsion. Preliminary experiments demonstrated that at the acid concentrations used, a centrifuging time of one minute at 3000 r.p.m. offered the best conditions for determining the rate of coagulation in 100-fold diluted latex. Experiments were made using acid concentrations of $N/10$, $N/20$, $N/30$, $N/40$, $N/60$, and $N/90$ sulphuric acid (based on total volume). Samples (25 cc.) of 50-fold diluted latex, containing 0.1152 gm. coagulable solids, were placed in 8-in. test tubes, 25 cc. of acid added from a burette, and the whole immersed in a thermostat at 30°C. $\pm$ 0.05°C. After appropriate time intervals samples were removed and centrifuged for one minute at 3000 r.p.m. The coagulum formed at the top in the form of a skin which was removed and placed on a weighed filter paper. Paper and coagulum were then dried in a vacuum oven at 60°C. for 30 min. and weighed.

Fig. 1 illustrates the results obtained from these experiments. With $N/90$ sulphuric acid, coagulation was negligible, whereas at a concentration of $N/10$ sulphuric acid, the emulsion was coagulated very quickly. At higher acid concentrations (not shown in the figure) the curves did not differ appreciably from that obtained with $N/10$ sulphuric acid. Thus $N/10$ and $N/90$ sulphuric acid may be taken as the limiting concentrations which define a region of slow coagulation. (It should be understood that this applies only to the centrifuging conditions and concentrations used in these experiments.)

The intermediate curves indicate that coagulation occurred in two stages. Addition of acid caused an immediate increase in particle size represented by

the portion of the curves from zero time to point A; from A to B a period of induction was apparent. At B the second stage commenced and the coagulation proceeded slowly and steadily. The sharp rise to A in all probability represented coagulation of the larger particles of the latex and it was only at B that all particles had grown to a size large enough to be centrifuged out.

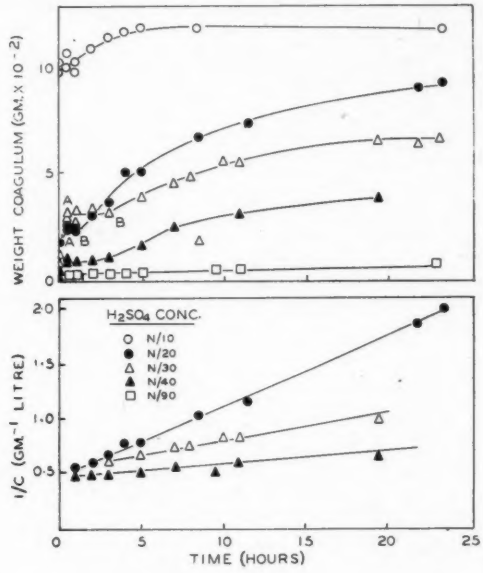

FIG. 1. Weight of coagulum formed vs. time. Variation of $1/C$ with time.

The portions of the curves beyond point B, for $N/20$, $N/30$, and $N/40$ acids, gave good linear relations when the reciprocal of the polymer concentration was plotted against time, indicating that coagulation occurred by a second order process. The rate constants, in gm.$^{-1}$ liter-hr., calculated from the slopes of these lines were 0.064, 0.029, and 0.012 for H^+ ion concentrations of 0.050, 0.033, and 0.025 gm. equiv. per liter respectively. From this it follows that the coagulation reaction may be represented by an equation of the form

$$[2] \qquad -\frac{dc}{dt} = k''c^2$$

where k'' is a function of the acid concentration. The rate constants proved to be linearly related to the concentration of the coagulating ion (Fig. 2). The line of Fig. 2 can be represented by the equation

$$[3] \qquad k'' = k'(H^+ - H_0^+)$$

where H_0^+ is the "threshold concentration", corresponding to the intercept

on the H^+ ion concentration axis. Combination of equations [2] and [3] gives

$$-\frac{dc}{dt} = k'c^2(H^+)'$$

where $(H^+)' = (H^+ - H_0^+)$. Integration of this equation gives

$$[4] \qquad c = \frac{c_0}{1 + k'c_0(H^+)'t}$$

where c_0 is the initial concentration of polymer. This expression gives the variation of c as a function of the initial concentration of polymer c_0, the acid concentration, and the time.

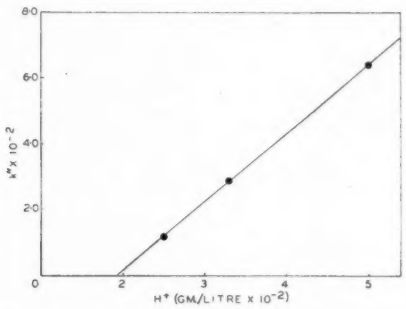

FIG. 2. Rate constant as a function of the H^+ ion concentration.

The value of H_0^+ from Fig. 2 is 1.92×10^{-2} gm. per liter. Below this concentration the coagulation rate should fall to zero. Experimentally, the value obtained for the minimum acid concentration necessary for coagulation is about 10^{-2} gm. per liter ($N/90$ sulphuric acid).

Surface Tension of Coagulating Latex

Heller and Oppenheimer (5) had noted that, during coagulation, the surface tension of latex emulsions decreased markedly, denoting an increase of soap in solution due to its desorption from the particles of the internal phase. They made no attempt to investigate this effect kinetically, however, and accordingly experiments were undertaken to compare the rate of desorption with the rate of coagulation.

The measurement of surface tension requires extreme precautions against contamination of the surface by impurities. In particular all glassware must be scrupulously cleaned, and this was accomplished by immersing it in concentrated nitric acid – sulphuric acid at 90°C. for two hours, washing thoroughly with redistilled water, steaming for 15 min., and finally rinsing again in redistilled water. A Cenco Du Nouy tensiometer was used for surface tension determinations. The platinum ring was flamed before and after each reading to ensure volatilization of any material collected on it. The temperature was

controlled at 30°C. ± 1°C. with a thermostatic jacket surrounding the Petri plate used to hold the samples.

A 20 ml. sample of latex, diluted 50 times with redistilled water, was poured into the Petri plate and to this was added 20 ml. of $N/10$, $N/15$, or $N/35$ sulphuric acid which, based on total volume, gave a 100-fold dilution of the latex and normalities of $N/20$, $N/30$, and $N/70$ for the acid. These solutions were then covered and allowed to stand without agitation. At various times the cover was removed and the surface tension measured. The surface was swept with a platinum wire a few minutes before each reading to remove flakes of coagulum from the surface.

The results of these experiments are illustrated in Fig. 3. It is seen that at all concentrations of acid used a large decrease in surface tension took place. The curves indicate that desorption of soap occurred for as long as 23 hr.

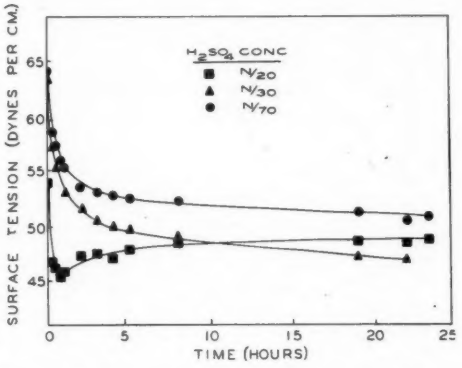

FIG. 3. Surface tension vs. time during coagulation.

Effect of Temperature

Data for coagulation at different temperatures (Table I) show that an in-

TABLE I

COAGULATION OF GR-S LATEX, TYPE II, AT DIFFERENT TEMPERATURES. 100-FOLD DILUTE LATEX AND $N/40$ H_2SO_4

Temperature (°C.)	Time (hr.)	Wt. coagulum (mgm.)
30	3.00	37.8
30	12.25	53.8
30	18.50	66.9
32	2.50	33.4
32	12.00	62.5
32	18.00	70.7
34	2.50	3
34	12.00	3

crease of temperature to 32°C. accelerated coagulation but further increase to 34°C. markedly stabilized the system. Treatment of latex at higher tempera-

tures in the presence of coagulating agents also resulted in stabilization of the particles (Table II). For example, latex to which has been added $N/40$ sul-

TABLE II

SUMMARY OF DATA FOR COAGULATION OF GR-S LATEX, TYPE II, AT DIFFERENT TEMPERATURES

Temperature T_1 (°C.)	Time (hr.) at T_1	Temperature T_2 (°C.)	Time (hr.) at T_2	Total time (hr.)	Weight coagulum (mgm.)
30	3	—	—	3	37.9
30	10	—	—	10	52.1
49	60	30	10	70	22.8
60	60	30	3	63	3.5
60	60	30	10	70	7.1
30	18	—	—	18	77.7
30	3	49	15	18	45.5
30	3	60	15	18	40.5

phuric acid was held for 60 hr. at 60°C. and then at 30°C. for three hours with the result that the weight of coagulated material was virtually negligible. Alternatively, if latex was coagulated at 30°C. for three hours, and then the temperature raised to 49°C., coagulation was again seriously retarded. Preheating of latex without addition of acid had no effect on either the coagulation velocity or the particle size.

It might be noted that Maron *et al.* (12) have also observed increased stabilization of latex with high temperature treatment in the presence of electrolytes, while critical phenomena of the type indicated above have been observed with soap solutions (17, 18, 20).

DISCUSSION

The equation derived for the coagulation of GR-S latex is

$$[4] \qquad c = \frac{c_0}{1 + k'(\mathrm{H}^+)'c_0 t}.$$

This equation is significant in that it bears a close resemblance to the Smoluchowski equation

$$[1] \qquad \sum_{j=1}^{\infty} n_j = \frac{n_0}{1 + k \epsilon n_0 t}$$

where $k = 4\pi DR$. It should be possible to obtain equation 4 as a particular case of equation 1. If the left-hand side of equation 1 is written as

$$\sum_{j=1}^{\infty} n_j = \sum_{j=1}^{m} n_j + \sum_{j=m}^{\infty} n_j$$

and if it is assumed that all particles $\geq n_m$ are removed by centrifuging, then $\sum_{j=1}^{m} n_j$ represents the concentration of particles remaining in the system. Further, m must be large since only particles of large mass are removed by the centrifuge, and therefore $\sum_{j=m}^{\infty} n_j$ must be small compared with $\sum_{j=1}^{m} n_j$. Neglecting the former, equation 1 becomes

$$\sum_{j=1}^{m} n_j = \frac{n_0}{1 + k \epsilon n_0 t}$$

which when transformed into weight concentrations gives

$$[5] \qquad \sum_{j=1}^{m} c_j = c = \frac{c_0}{1 + k'''\epsilon_0 c_0 t}.$$

In the Smoluchowski equation k is the rate constant for coagulation of uncharged particles. For partially charged particles it is multiplied by ϵ. Since $k = 4\pi DR$ is the rate constant when all collisions are effective, it is essentially the collision number, and the rate can be expressed by analogy with chemical kinetics as

$$\text{Rate constant} = Ze^{-E/RT}$$

where $Z = k = 4\pi DR$, and $e^{-E/RT} = \epsilon$ expresses the fraction of effective collisions, that is the fraction of collisions in which the colliding particles have enough kinetic energy to overcome the repulsive forces of the partially neutralized particles. From Fig. 2 it is evident that $\epsilon = e^{-E/RT}$ is a linear function of the effective H^+ ion concentration and may be put equal to $k''(H^+)'$. Substituting in equation 5 gives

$$c = \frac{c_0}{1 + k'(H^+)'c_0 t}$$

which is equivalent to equation 4.

Hence, it appears that coagulation of GR-S latex exhibits the same characteristics as coagulation of a monodisperse sol, to which the Smoluchowski equation is applicable. The portion from zero time to point A in the curves of Fig. 1 represents an initial fast coagulation of all particles. In this initial agglomeration of particles the aggregates appear to be loose, and require time to reach equilibrium stability. The section OB of the curves exhibits a large degree of irregularity. The experiments are difficult to reproduce and the results are semiquantitative only, but they suggest an initial unstable aggregation, from which portions of the particles may detach themselves and diffuse away. This is in agreement with the suggestion of Lewis (10) that coagulating particles adhere initially to each other without immediate coalescence. At B, the products presumably have attained internal equilibrium and the coagulation proceeds smoothly from this point.

The soap desorption accompanying the coagulation exhibits the properties of a rate process (Fig. 3) and it is interesting to enquire into the mechanism of this effect.

The amount of emulsifier which can be adsorbed by the suspended particles is clearly a function of the extent of surface of the particles, and the decrease in surface area when coagulation occurs should lead to a desorption of the emulsifier molecules (or ions) from the surface. The surface area of the particles as a function of time may be calculated from the Smoluchowski equation, and if it is assumed that the number of adsorbed molecules, σ, per unit surface area remains constant, the number of molecules desorbed will be given by the difference between the surface area of the particles at zero time and at time t multiplied by σ. Thus if k particles each of radius r_1 and volume v_1 with total

volume $4/3\pi r_1^3 k$ coalesce to form one particle of radius r_k and volume $4/3\pi r_k^3$, the radius r_k is equal to $k^{1/3} r_1$. If n_k denotes the concentration of k-particles, the surface area of a k-fold particle is $4\pi k^{2/3} r_1^2 n_k$. The number of particles n_k as a function of time is given by the Smoluchowski equation as

$$\frac{n_0(at)^{k-1}}{(1+at)^{k+1}}$$

where $a = 4\pi DRn_0\epsilon$. By summing over the k's and letting $\alpha = at/(1+at)$, the total surface area of the suspended particles is obtained:

$$[6] \qquad S_T = \frac{4\pi r_1^2 n_0}{(1+at)^2} \sum_{k=1}^{\infty} k^{2/3} \alpha^{k-1}.$$

The number of molecules removed from the surface of the particles during coagulation is then given by

$$[7] \qquad \begin{aligned} c &= \sigma(S_0 - S_T) \\ &= c_0 - \sigma \frac{4\pi r_1^2 n_0}{(1+at)^2} \sum_{k=1}^{\infty} k^{2/3} \alpha^{k-1} \end{aligned}$$

which may be written as

$$[8] \qquad c_0 - c = \sigma \frac{4\pi r_1^2 n_0}{(1+at)^2} \sum_{k=1}^{\infty} k^{2/3} \alpha^{k-1}.$$

The series in equation 8 cannot be evaluated analytically; in the range of small α,* however, the series converges rapidly and to a reasonable approximation, neglecting higher terms,

$$[9] \qquad c_0 - c = \sigma \frac{4\pi r_1^2 n_0}{(1+at)^4} (1 + 3.6\, at).$$

For moderate concentrations of emulsifier the surface tension can be represented by

$$[10] \qquad \log \gamma = b \log(c_0 - c) + \log m$$

where b and m are constants. Substitution for $c_0 - c$ in equation 10 and appropriate expansion of the logarithms gives the relation

$$[11] \qquad \log \gamma = A - B \log t.^{**}$$

Fig. 4 is a plot of $\log \gamma$ against $\log t$. The agreement between the predicted linearity and the experimental behavior is probably adequate, in view of the approximations involved in the calculations and the accuracy of the experimental work.

To account for the observed stabilization effect with change of temperature, consideration may be given to the soap adsorbed on the latex particles, in

* *If values for the "molecular weight" of the latex particles and of E are taken as 600,000 and 7 kcal. respectively, both of which seem reasonable enough, α is readily calculated to be of the order 10^{-2}.*

** *For certain values of α the summation may be replaced by an integration, and it can be shown that the same relation between γ and t is obtained.*

solution, and in micellar form. These three forms are in equilibrium and can be represented by the following scheme:

$$\underset{C_A}{\text{adsorbed soap}} \underset{(A)}{\overset{k_1}{\underset{k_2}{\rightleftarrows}}} \underset{C_F}{\text{free soap}} \underset{(B)}{\overset{k_3}{\underset{k_4}{\rightleftarrows}}} \underset{C_M}{\text{micellar soap.}}$$

Under normal conditions, when most of the soap is adsorbed, k_2 is greater than k_1. Above the critical concentration for micelle formation (14), k_3 is much greater than k_4, and any added soap increases the micelle concentration without altering the concentration of free soap. Also, k_2 is greater than k_3 since when soap is added to the emulsion it is adsorbed by the particles and surface saturation of the particles is attained at the critical concentration for micelle formation (11). However, since the processes of micelle formation and adsorption are similar, it may be assumed that k_2/k_3 will be less than k_2/k_1.

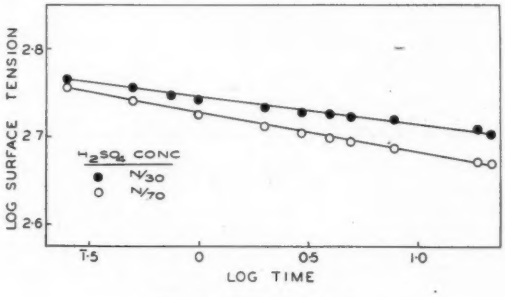

FIG. 4. Log γ vs. log t.

When coagulating agent is added to the emulsion, the critical concentration for micelle formation is lowered (2, 14). This results in an increase of K_3, the equilibrium concentration for process B, and in k_3, since $K_3 = k_3/k_4$. Consequently the concentration of free soap C_F is decreased, and soap is desorbed from the particles to readjust the equilibrium K_A. This desorption leads to coagulation, with an attendant decrease in surface. However, a decreased surface for adsorption will increase K_A since less surface is presented to the emulsifier and therefore the decreased surface leads to a further desorption of soap. The extent to which the soap is removed from solution into the micelles will depend on the relative magnitudes of k_2 and k_3. As the decrease of surface increases the concentration of free soap in solution, the rate of coagulation will be controlled by the rate of removal of this soap into the micelles; if this free soap is not removed it will prevent further coalescence, since the rate of adsorption k_2C_F will increase. The rate of removal of soap by micellization is k_3C_F, and thus to have coagulation k_3 must be greater than k_2. k_3 depends on the decrease of critical concentration resulting from addition of coagulating agent, and therefore the coagulation velocity can be associated with the effect of the coagulating agent on the critical concentration.

The critical temperature effect is particularly interesting when viewed in this way, and may be explained by the effect of temperature on the rate constants. Increased temperature causes an increase in the critical concentration for micelle formation (8) and this effect is more marked in the presence of electrolytes (20). An increase in temperature also results in a decrease in adsorption, i.e. k_1 and k_4 are increased. At the critical temperature when the micelles break up, there is a sharp increase in C_F, the free soap, which is available for stabilization of the latex particles by adsorption, and coagulation is thus arrested.

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PHTHALIDE FORMATION

II. CONDENSATIONS WITH 3-HYDROXY-4-METHYLBENZOIC ACID[1]

By E. H. Charlesworth, H. J. Anderson, and N. S. Thompson

ABSTRACT

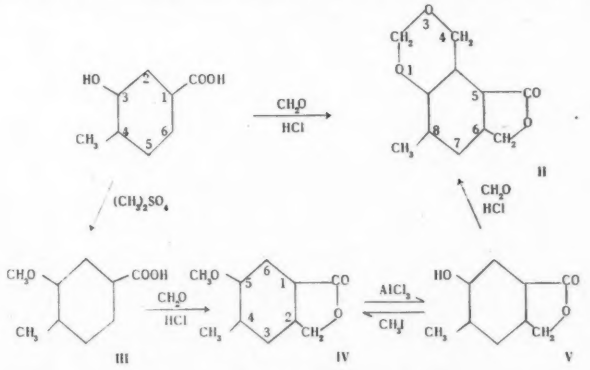
The condensation of 3-hydroxy-4-methylbenzoic acid with aqueous formaldehyde and hydrochloric acid yields the lactone of 6-hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic acid. This dioxanylphthalide has also been produced in a similar type of condensation from 5-hydroxy-4-methylphthalide which can be obtained by demethylation with aluminum chloride of 5-methoxy-4-methylphthalide.

Proof of the presence of the *m*-dioxane and phthalide rings in the condensation product has been obtained by opening these rings in succession. The action of alkaline permanganate opens the phthalide ring to yield a substituted phthalic acid. Acid hydrolysis then opens the *m*-dioxane ring with loss of formaldehyde and the formation of a new phthalide ring. Successive steps of decarboxylation, methylation, and oxidation of the new phthalide yield the known 3-methyl-4-methylphthalic acid.

INTRODUCTION

The literature contains a fairly extensive number of condensations in which methoxy-substituted benzoic or toluic acids have been condensed with formaldehyde and hydrochloric acid to yield phthalides or in some cases chloromethylphthalides. Condensations with the corresponding hydroxy-substituted acids are on the other hand comparatively rare, the explanation presumably being that in most cases only amorphous high melting products of diphenylmethane or Bakelite structure are isolated.

When 3-hydroxy-4-methylbenzoic acid (I) is condensed in the usual manner with formaldehyde and hydrochloric acid, a crystalline compound (m.p. 165°C.) is obtained. This product has been identified as the lactone of 6-hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic acid (II).



The structure of this dioxanylphthalide (II) is supported by the following

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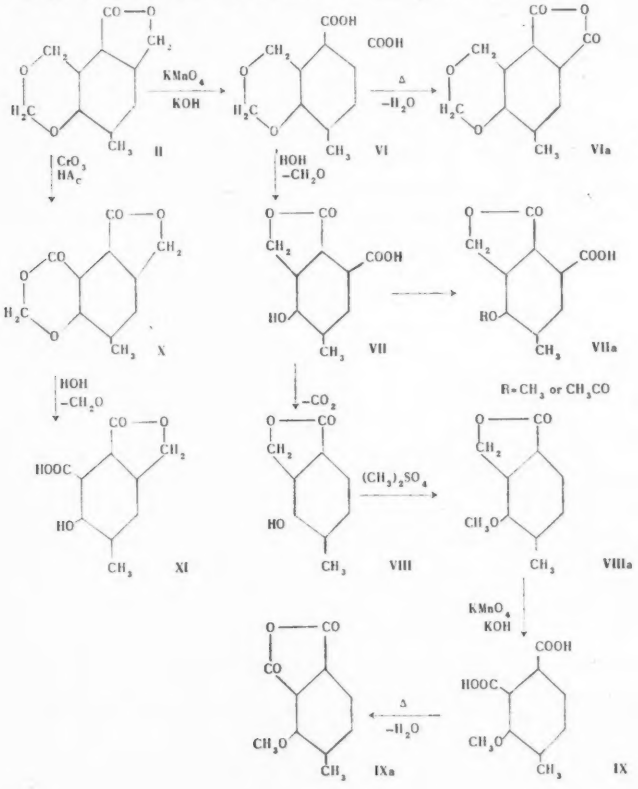
Contribution from the Department of Chemistry, The University of Manitoba, Winnipeg, Manitoba.
For Part I in this series, see Can. J. Research, B, 23: 17. 1945.

alternative synthesis. 5-Methoxy-4-methylphthalide (IV) was prepared from 3-methoxy-4-methylbenzoic acid (III) by the method of Charlesworth, Rennie, Sinder, and Yan (7). By demethylation of IV with hydriodic acid or better with aluminum chloride (anhydrous) in dry benzene the hydroxyphthalide (V) was obtained. Tests indicated that the demethylating agents had not broken the phthalide ring and this was proved by remethylation to the methoxyphthalide (IV) by the method of Irvine (9). When the hydroxyphthalide (V) was condensed with formaldehyde and hydrochloric acid, a product identical with the dioxanylphthalide (II) was obtained, thus completing the cycle. This substance (II) gave a stong fluorescence in the phthalide test with resorcinol and sulphuric acid. It gave also a reddish-orange precipitate with phloroglucinol and sulphuric acid which Mehta and Ayyar (10) have used as a test for the *m*-dioxane ring.

The presence of the *m*-dioxane and phthalide rings in II has been shown by degradative oxidation following the classical methods of Borsche and Berkhout (1) and more recently of Buehler and his coworkers (2, 3, 4, 5, 6). Oxidation of II with alkaline permanganate opened the phthalide ring and gave the ortho dibasic acid (VI) which readily formed the anhydride (VI*a*).



Acid hydrolysis of VI opened the dioxane ring with elimination of formaldehyde and the formation of the hydroxylactone (VII). Decarboxylation with quinoline and copper chromite gave the hydroxyphthalide (VIII). Oxidation of the methyl ether (VIII*a*) with alkaline permanganate opened the new phthalide ring and yielded the dicarboxylic acid (IX) whose orientation has been previously established by Simonsen and Rau (11).

When the dioxanylphthalide (II) was oxidized with chromic oxide and acetic acid the methylene ether – ester (X) was produced. This is the usual first step in the opening of *m*-dioxane rings. Alkaline hydrolysis of this ether–ester according to the method of Borsche and Berkhout (1) splits off formaldehyde, but the acid (XI) has not yet been isolated in pure form.

EXPERIMENTAL

3-Hydroxy-4-methylbenzoic acid (I), 3-methoxy-4-methylbenzoic acid (III), and 5-methoxy-4-methylphthalide (IV) were made as described by Charlesworth, Rennie, Sinder, and Yan (7) in the first paper in this series.

The Lactone of 6-Hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic Acid (*II*)

3-Hydroxy-4-methylbenzoic acid (20 gm.), formaldehyde solution (100 ml., 40%), and concentrated hydrochloric acid (100 ml.) were heated on the water bath for one hour. The acid did not appear to go into solution, but a definite reaction occurred. After cooling and dilution, the solid product was filtered and washed with water. It was crystallized from alcohol from which it separated as fine white needles (14 gm.) melting sharply at 165°C. Found: C, 63.9; H, 4.86%; mol. wt. (Rast method), 195; neut. equiv., 201. Calc. for $C_{11}H_{10}O_4$: C, 64.0; H, 4.86%; mol. wt., 206; neut. equiv., 206. On warming this substance with resorcinol and concentrated sulphuric acid followed by sodium hydroxide solution, the greenish fluorescence characteristic of the phthalide ring developed. When warmed with phloroglucinol and strong sulphuric acid a reddish precipitate was formed which Mehta and Ayyar (10) have used to confirm the presence of the *m*-dioxane ring.

5-Hydroxy-4-methylphthalide (*V*)

This product was produced by demethylation of the corresponding methoxyphthalide (IV). Two methods were employed:

(*a*) Hydriodic acid (27 ml., sp.gr. 1.7) and acetic anhydride (27 ml.) were carefully mixed in an atmosphere of carbon dioxide and added to a mixture of 5-methoxy-4-methylphthalide (2 gm.) and washed and dried red phosphorus (2 gm.). The mixture was refluxed gently for three hours in an atmosphere of carbon dioxide, cooled, diluted with water, and filtered to remove phosphorus. The filtrate was evaporated under reduced pressure by a slow current of carbon dioxide. A resinous precipitate formed, which on crystallization from alcohol gave a small amount of a white crystalline solid melting at 190–195°C.

(*b*) More successful results were obtained employing the method introduced by Fernholz and Finkelstein (8) using anhydrous aluminum chloride.

5-Methoxy-4-methylphthalide (1.8 gm.), anhydrous aluminum chloride (1.4 gm.), and dry benzene (40 ml.) were heated on a water bath. After refluxing for eight hours the brown oil, which had settled out slowly, solidified. After cooling, this solid material was broken up, filtered, and washed first with benzene and then with water. On crystallization from alcohol it separated in fine white needles (0.6 gm.), which melted at 195–197° and were identical with the product formed by method (*a*). Further recrystallization raised the melting point to 205°C. The compound was soluble in hot water and very soluble in hot alcohol, ether, acetone, and benzene. It yielded a strong phthalide test with resorcinol and sulphuric acid. Found: C, 65.7; H, 5.02%. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.88%.

5-Methoxy-4-methylphthalide (*IV*)

A mixture of 5-hydroxy-4-methylphthalide (0.2 gm.), dry silver oxide (0.5 gm.), and methyl iodide (10 gm.) was refluxed gently for an hour. The excess methyl iodide was removed by distillation and the residue extracted with hot alcohol. The extract was concentrated and, on cooling, glistening white needles which melted at 143–146°C. separated. A mixed melting point proved the substance identical with 5-methoxy-4-methylphthalide, produced by direct condensation of 3-methoxy-4-methylbenzoic acid with formaldehyde and hydrochloric acid (7).

Condensation of 5-Hydroxy-4-methylphthalide

A mixture of 5-hydroxy-4-methylphthalide (0.5 gm.), formaldehyde solution (5 ml., 40%), and concentrated hydrochloric acid (8 ml.) was heated for an hour on the water bath. After cooling and dilution the solid was filtered off. It crystallized from alcohol in the form of needles (0.4 gm.), which melted at 164–165°C. and which mixed melting point showed to be identical with the lactone of 6-hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic acid described above.

1,3-Benzodioxane-8-methyl-5,6-dicarboxylic Acid (*VI*)

The dioxanylphthalide II (6.0 gm.) was dissolved in potassium hydroxide (10 gm.) in water (300 ml.) by allowing the mixture to stand overnight. The solution was cooled in an ice bath to 5–10°C. and maintained at this temperature during the oxidation. A solution of potassium permanganate (24 gm.) in water (700 ml.) was added slowly over a period of one hour. The resulting green solution was allowed to regain room temperature and to stand overnight. The manganese dioxide was filtered off, washed with water, and the combined filtrates acidified with hydrochloric acid, litmus being employed as indicator. The solution was concentrated to about 300 ml. by evaporation on a hot plate at 80°C. and acidified with hydrochloric acid, with Congo red as indicator. The white, chalky, crude acid was separated by filtration and purified by dissolving in sodium bicarbonate and treating with Norite. On acidification a sufficiently pure acid (4.0 gm.) was obtained for further reactions. It was recrystallized for analysis from acetone. The pure acid melted at 199–200°C. with loss of water. Found: C, 55.3; H, 4.17%; neut. equiv., 120. Calc. for $C_{11}H_{10}O_6$: C, 55.5; H, 4.20%; neut. equiv., 119.

The Anhydride of 1,3-Benzodioxane-8-methyl-5,6-dicarboxylic Acid (VIa)

The aforementioned acid VI (1.1 gm.) was heated on an oil bath at 202–205° until the violent evolution of water vapor had subsided. Continued heating or higher temperature was avoided, as it caused evolution of formaldehyde and resin formation. The solidified mass was extracted with boiling toluene and filtered hot. On cooling, the anhydride separated in masses of yellow needles (0.5 gm.). A second crystallization from toluene gave a pure product which melted at 193–194°C. Found: C, 60.0; H, 3.69%. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.64%.

The anhydride can also be formed by dissolving the acid (1.2 gm.) in hot acetic anhydride (1.9 ml.). The solution was evaporated to half its volume on the hot plate and, on cooling, crystals of the anhydride separated. These were filtered, washed with anhydrous ether, and crystallized as before from toluene.

The Lactone of 3-Hydroxymethyl-4-hydroxy-5-methyl-1,2-phthalic Acid (VII) and Its Derivatives (VIIa)

The dicarboxylic acid VI (6.0 gm.) was heated under reflux for six hours with concentrated hydrochloric acid (100 ml.) and water (100 ml.). Formaldehyde was evolved during the heating. The yellow needles formed were collected and recrystallized from a mixture of alcohol and petroleum ether. The recrystallized material (4.5 gm.) melted at 269–270°C. Found: C, 57.4; H, 3.87%; neut. equiv., 200. Calc. for $C_{10}H_8O_5$: C, 57.7; H, 3.84%; neut. equiv., 208.

The 4-methyl ether of this acid was formed by treatment in the usual manner in sodium hydroxide solution with dimethyl sulphate. It crystallized from acetone in fine white needles which melted at 154–155°C. Found: C, 59.3; H, 4.71%. Calc. for $C_{11}H_{11}O_5$: C, 59.4; H, 4.50%.

The 4-acetyl derivative of the above acid was prepared in the usual manner by treatment of the potassium salt with acetic anyhydride. The crude acetate was crystallized first from alcohol and then from acetone. The purified material melted at 189–190°C. Found: C, 57.5; H, 4.02%. Calc. for $C_{12}H_{10}O_6$: C, 57.6; H, 4.03%.

3-Hydroxy-4-methylphthalide (VIII)

The monocarboxylic acid VII (4.8 gm.) was dissolved in pure quinoline (40 ml.) and copper chromite (0.01 gm.) added. The mixture was heated on an oil bath at 185°C. as long as carbon dioxide was evolved. The cooled quinoline solution was acidified with dilute hydrochloric acid (1 : 1) and extracted with ether. Removal of the ether left a yellow oily material which was purified by repeatedly treating the solution in dilute sodium hydroxide with Norite. After acidification the recovered phthalide (2.1 gm.) was crystallized from water and melted at 190–191°C. Found: C, 65.6; H, 4.84%. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.88%.

3-Methoxy-4-methylphthalide (VIIIa)

The 3-methyl ether of the phenolic phthalide (VIII) was obtained by repeated methylation with methyl sulphate and sodium hydroxide. After acidification and several crystallizations from a mixture of acetone and water

it melted at 119–120°C. Found: C, 67.0; H, 5.60%. Calc. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.62%.

3-Methoxy-4-methylphthalic Acid (IX)

3-Methoxy-4-methylphthalide (1.1 gm.) was dissolved in sodium hydroxide solution (10 ml., 10%). To this stirred solution finely powdered potassium permanganate (1.0 gm.) was added gradually at such a rate that the temperature did not rise above 22°C. The solution was allowed to stand at room temperature for 24 hr. The manganese dioxide was decomposed by the gradual addition of sodium bisulphite and after acidification the solution was extracted thoroughly with ether. The white solid left after removal of the ether was triturated with sodium bicarbonate solution. A residue (0.3 gm.) of unoxidized phthalide was left. The bicarbonate solution was treated with activated charcoal, filtered, and acidified with hydrochloric acid. The acid thus obtained was crystallized thrice from water and finally from a mixture of acetone and chloroform from which it separated in small prisms (0.3 gm.) which melted at 172–173°C. Found: C, 57.1; H, 5.07%. Calc. for $C_{10}H_{10}O_5$: C, 57.1; H, 4.76%. A mixed melting point of this acid with an authentic sample prepared by the method of Simonsen and Rau (11) gave no depression.

The Anhydride of 3-Methoxy-4-methylphthalic Acid (IXa)

When the dibasic acid (IX) was heated at 160° on an oil bath until bubbling ceased, the anhydride was produced. When recrystallized from toluene it melted at 133–134°. Simonsen and Rau (11) reported a melting point of 135°C. A mixed melting point with a sample prepared by the method of these authors confirmed the identity of the above anhydride.

The Lactone of 6-Hydroxymethyl-8-methyl-1,3-benzodioxane-4-one-5-carboxylic Acid (X)

The dioxanylphthalide II (2.0 gm.) was dissolved in warm glacial acetic acid (12 ml.) and the solution allowed to regain room temperature. A saturated solution of chromium trioxide (3.0 gm.) in water was diluted with glacial acetic acid (5 ml.) and gradually added to the phthalide solution at such a rate that the temperature did not exceed 70°. The mixture was allowed to stand at room temperature for 36 hr., heated to 50° on the hot plate, and again cooled. After four hours it was diluted with water (250 ml.) and allowed to stand overnight. The precipitate was removed by filtration, washed thoroughly with water, dried, and extracted with cold acetone (50 ml.) which removed any unreacted dioxanylphthalide. The residue was dissolved in the minimum of boiling acetone and filtered. Two thirds of the acetone was evaporated and on cooling, white crystals which melted at 240–245°C. were obtained. A further crystallization from acetone and finally from water afforded a pure product (0.12 gm.) which melted at 249–250°C. Found: C, 59.9; H, 3.67%; mol. wt., 211. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.64%; mol. wt., 220.

When the above methylene ether – ester (X) was hydrolyzed on the water bath with 20% sodium hydroxide solution a strong odor of formaldehyde was noticed, but the ortho hydroxy acid (XI) has not yet been isolated in pure form.

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THE DIELECTRIC BEHAVIOR OF VAPORS ADSORBED ON SILICA GEL[1]

By J. A. Snelgrove,[2] H. Greenspan,[3] and R. McIntosh[4]

ABSTRACT

Experiments to determine the dielectric constants of adsorbed butane, ethyl chloride, and water on an activated silica at frequencies up to 3.7 Mc. per sec. are reported. No Debye-type dispersion was observed for the polar adsorbates down to −30° C., the lowest temperature employed. Mixtures of ethyl chloride and water, and of butane and water, were also studied. The assumption that adsorption of ethyl chloride and water occurs with both adsorbates sharing two types of sites sufficed to explain the findings for this system. No explanation was apparent to account for the behavior of the butane–water system.

Formulae due to Kurbatov and to Snelgrove and McIntosh have been used to interpret the results obtained with polar adsorbates. On the assumption that the adsorbates have densities equivalent to those for the liquid state at the same temperature, it is concluded that adsorbed water undergoes oscillatory motion. The first quantities of ethyl chloride adsorbed behave as though the molecules may rotate freely within an angle of 98°. The ethyl chloride adsorbed nearer the saturation pressure shows oscillatory motion, as a negligible temperature coefficient of the molar polarization is observed.

INTRODUCTION

In previous publications (5, 6), data have been presented which are characteristic of the dielectric behavior of water, ethyl chloride, and butane when adsorbed on a porous silica gel. It was shown that for all the adsorbates linear sections of the plots of capacitance change vs. volume adsorbed were obtained; that the several linear sections for each substance indicated an abrupt alteration of the electrical properties of the adsorbed material; and that the apparent change of electrical properties occurred at a quantity of adsorbate on the surface which did not vary with temperature for a given adsorbate and which did not appear to be related to the cross-sectional area of the adsorbed species. In addition, up to a frequency of 100 kc. per sec., no Debye-type dispersion was found down to −15°C. in the case of adsorbed water, and −30°C. in the case of ethyl chloride.

An explanation of the sudden change of dielectric properties was sought. There was no particular support for the view expressed by Kurbatov (3) that the observed change marks the completion of the unimolecular layer. The phenomenon was therefore attributed to adsorption on different types of site, and the density of the adsorbed phase was assigned a value which would yield a "reasonable" absolute value of the polarization.

Other unexpected results were observed. The temperature coefficient of the dielectric constant of the polar adsorbates was found to have anomalous values when compared with bulk (liquid) matter. Moreover, the behavior

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exhibited differed for each linear section along an isotherm. The most difficult observation to explain was the high apparent value of the polarization, indicating a contribution from the orientational part to the total polarization, in combination with a zero or very small temperature coefficient. It was pointed out that this difficulty could be avoided through the assignment of the density of the adsorbate. Such a practice, however, is not particularly helpful in extending our knowledge of the adsorbed state, and indeed, would have to be abandoned as soon as the knowledge of this factor is obtained. Information concerning the density of the adsorbate can already be derived for nonpolar materials (6) and at sufficiently high frequencies the same method could be applied for polar adsorbates.

In the present paper measurements are reported similar to those referred to, but the frequency range has been extended to 3.7 Mc. per sec. This is about the upper limit which can be investigated using the form of cell and housing which has been developed. The difficulty arises from errors introduced by leads. As the electrical system, once calibrated, is quite satisfactory up to this frequency, a description of the system will be given.

Using this apparatus three chief findings were made. First, the dielectric loss factor, while increasing at the higher frequencies, did not appear to be near a maximum, although the higher frequency range permitted a better elimination of the contribution of d-c. conductance to the loss tangent in the case of water than had previously been achieved.

Second, mixtures of adsorbed ethyl chloride and water may be treated as adsorbing on two types of site, both adsorbates competing for the two types of site. Alternatively, the adsorption data are shown to be consistent with the equation given by Tompkins (8) for adsorption on a heterogeneous surface which possesses a very wide distribution of the energies of the sites. If this view is adopted, it may be seen that both water and ethyl chloride are distributed over the various types of site in the same way.

Third, the adsorption of butane and water has presented a result for which we can offer no explanation. It is found that the position of the abrupt change of slope from one linear section to the next for butane isotherms on gel with varying quantities of water is displaced up to a limiting quantity of water added. Beyond this quantity no further displacement is observed, a behavior quite different than that of ethyl chloride adsorbed on gel of various water contents. In addition, it is also found that the equilibrium pressure of the butane, for any given quantity adsorbed, continues to increase with additional water in the gel.

Some reinterpretation of results reported earlier is attempted. This is based on formulae which are now available, and which express the orientational polarization of an oscillating dipole and a dipole which is free to rotate within a given cone angle, but cannot rotate through larger angles. Kurbatov (4) developed expressions for the polarizations of such molecules when oscillation or rotation may take place in three dimensions. In the following paper (7) the cases of dipoles restricted to oscillate or rotate in the plane of the adsorbing

surface are considered. The importance of the model of an oscillating dipole is the prediction of a zero temperature coefficient of the polarization, although the contribution from the orientational polarization need not be zero. Thus some of the effects attributed to the density may now be explained in terms of the oscillating dipole. A rotating dipole shows a temperature coefficient of the polarization. Information now available is not sufficient to state that the model of the oscillator is to be preferred to density adjustment, or vice versa. The oscillator model offers greater specificity, and, in conjunction with the detection and study of Debye dispersion, should assist greatly in the interpretation of dielectric measurements.

EXPERIMENTAL

The adsorption assembly, cell, and pressure gauges have been adequately described (6), and need not be shown in detail here. However, a somewhat novel and very convenient arrangement was used for the measurement of the amount of water adsorbed. It is shown diagrammatically in Fig. 1. The

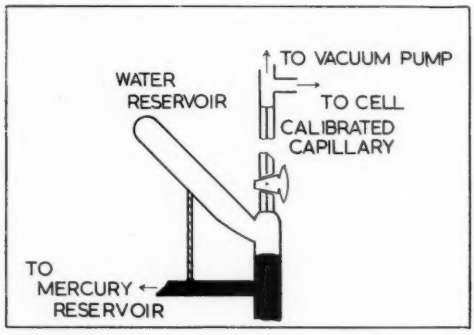

FIG. 1. Diagram of water doser.

design has the advantage that the water need be freed of dissolved gases only once, and a single filling is sufficient for many experimental runs. The mercury displaces water into the calibrated capillary, which is then isolated by means of the stopcock from the main volume, eliminating the need of temperature regulation. The level is read by means of a telescope and a Beckmann thermometer scale, and the desired amount of water is allowed to distill into the cell. To prepare for a new addition, it is only necessary to lower the mercury below the side-arm, allowing some of the trapped water to enter the capillary, and then raise it again to the desired level. Usually a difference in height of about 5 cm. of capillary was used, and the volume of material adsorbed for a single admission was known to $\pm$ 0.3%. No correction was needed for the residual water vapor in the connecting lines over the low relative pressure range investigated.

Measurement of Capacitance Change

The bridge system employed for measurements up to 100 kc. per sec. has

already been described (6). A resonance circuit was used above this frequency. It consisted of a coil, the measuring condenser and the test cell in parallel with one another and with the coil, and a vacuum tube voltmeter connected across the common terminals of the circuit. A high resistance in series with the grid of the voltmeter tube assured negligible current drain by the voltmeter branch even at high frequencies. Neither of the condensers of the mesh was free from residuals, and these were sufficient to cause significant errors at the higher frequencies. The effect of the residuals was also dependent upon the setting of the condenser, in the case of the measuring condenser, and the value of capacitance of the test condenser. The measuring condenser, a General Radio Type 722, was found to have an apparent capacity, which could be related to its true, or low frequency value of capacity, by the relation

$$C_a = C_t(1 + \omega^2 L C_t)$$

where L is the series inductance of the condenser, C_a and C_t are the apparent and the true value of the capacitance, respectively.

Now if the reading of this measuring condenser is determined at resonance, and if any change is brought about in the capacitance of the test cell branch, a new setting of the measuring condenser is required to re-establish resonance. The difference between any two such readings may be corrected by the above formula to yield the true value of the capacitance change which occurred. However, the measured change thus obtained arises from the condenser in the test arm and the effect of residuals of that condenser. It was therefore necessary to obtain the values of the inductance and capacitance of the leads of the test cell. The capacitance of the leads, including the connections through the cell housing, was determined over the frequency range and varied from 48.82 to 48.25 $\mu\mu$f. The effect of the series inductance and resistance of the leads on the capacitance of known condensers, of values covering the range expected with the test cell, was determined at various frequencies. The apparent capacitance was expressed in terms of the true by means of the formula given above. This practice resulted in values of L_T, where this is the series inductance of the test cell, which varied slightly both with frequency and value of the condenser at the end of the leads. As the variation was slight, showing that the effect of the series resistance was small, the procedure was adopted of using a value of L_T which was appropriate to the frequency and value of capacitance of the test cell. Under the worst conditions, that is a high capacitance at the end of the leads and at the highest frequencies, the correction term was about 70 $\mu\mu$f. in about 600 $\mu\mu$f. for the test cell. Application of the correction reduced the error to less than 1 $\mu\mu$f. It may be added that over the frequency range where both the bridge and resonance systems could be employed, the data obtained agreed within 0.1 $\mu\mu$f.

The variation of the equivalent shunt conductance of the test cell branch was determined by evaluating the conductance of the circuit when only degassed adsorbent was in the cell and when a known quantity of adsorbate had been added. The standard method of obtaining the conductance from the shape of the resonance peak was employed. The change of conductance

for a given addition of adsorbate can then be considered as arising from the connection of a condenser across the test branch, the capacitance of which is that caused by the addition of the adsorbate, and the shunt conductance of which is that necessary to account for the observed conductance change. In the present investigation the changes of conductance were very small, and the total shunt conductance of the composite dielectric is reported.

These procedures are applications of the principles discussed by Hartshorn and Ward (2).

Oscillator and Vacuum Tube Voltmeter

The signal was supplied by a series-fed Hartley oscillator, employing a 6J5 tube, and having a frequency range from 0.100 to 3.70 Mc. per sec. It was operated at fixed and calibrated frequencies, obtained by changing the coil of the tank circuit or by varying the tuning condenser. The oscillator was coupled to the resonant circuit by means of a cathode follower circuit, employing a 6J5 tube and a coil. The cathode follower served to isolate the oscillator. A regulated power supply was used.

The voltage across the resonant circuit was measured by means of a bridge-type vacuum tube voltmeter (2) in conjunction with a moving coil galvanometer having a sensitivity of 0.0029 μamp. per mm. The self-compensating action of the bridge-type circuit, the use of type 957 tubes of low interelectrode capacitance, and the use of batteries as power source enabled the optimum sensitivity of the galvanometer to be utilized.

Results with Water

The increased frequency at which the electrical properties of the adsorbed water were measured resulted in little new information. The main finding arising from measurements made at 0.6° C. was that some conduction dispersion was apparent in the results obtained up to 0.1 Mc. per sec. which were reported earlier. This dispersion led to slightly high values of the polarization. Whereas values of the polarization per cubic centimeter of 1.047 and 0.952 have been reported for the first and second linear sections respectively using formula (*a*) of the paper by McIntosh, Rideal, and Snelgrove (6), these should be reduced to 1.02 and 0.900 as determined from the measurements at higher frequencies. In view of the difficulty of interpreting results, this change does not alter materially what can be deduced concerning the adsorbed state of water. As pointed out previously (6), a value of the polarization per cubic centimeter greater than one is not an absurdity, since an incorrect assignment of the density of the adsorbate can account for such values. The values stated here are based upon a density of 1.0 gm. per cc.

The high polarization per cubic centimeter along both linear sections, in conjunction with a zero temperature coefficient, may now be interpreted by means of the models of oscillating dipoles. The choices are either a dipole which may oscillate in three dimensions, or a dipole which oscillates in the plane of the adsorbing surface. The correction factor a of the Kurbatov formula (4), or of the formula given in the following paper (7), may be evaluated by employing the known refractive index of water and the value of its

permanent dipole moment of 1.87 debyes. On this basis the value of a is 0.159 along the second linear section, where it is possible to assign the normal liquid density. The two formulae yield respectively 5.9 and 1.1 for β^2. These values lead to 3400 cal. per mole and 640 cal. per mole, respectively, for the energy of the oscillator. Here β^2 is $\omega^2 I/2kT$ where ω is the frequency of oscillation and I is the moment of inertia of the dipole. E is $\omega^2 I/2$.

Since it has been pointed out by De Boer (1) that a physically adsorbed polyatomic molecule should lie flat on the surface, the values for the oscillator constrained to the plane would appear preferable.

If measurements can be obtained at sufficiently high frequencies for ω to be determined, since the orientational polarization observed leads to $\mu^2/\omega^2 I$, a comparison of μ^2/I between molecules in the adsorbed state and in the gaseous state should be possible.

One further result of the tests at higher frequencies is the recognition that Debye-type dispersion is just becoming discernible for moderate quantities of adsorbed water. As shown in Fig. 2, where the loss tangent of the composite

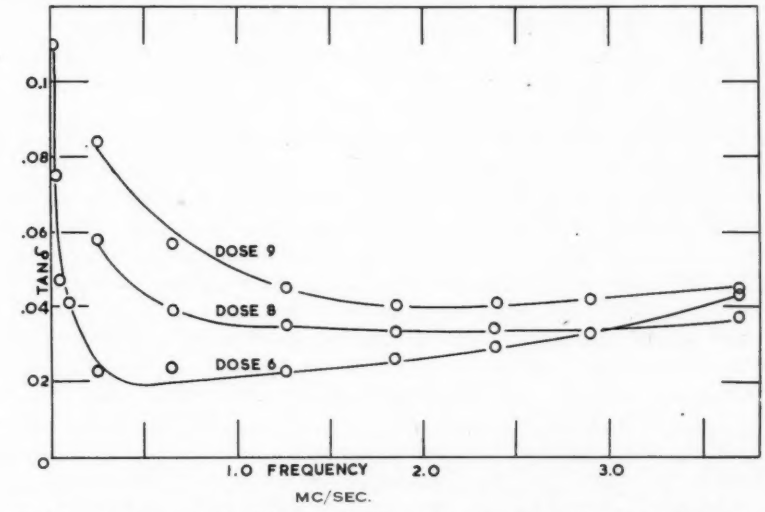

FIG. 2. Loss tangent of cell filled with silica and various quantities of adsorbed water.

dielectric is plotted against frequency, a minimum is observed for the sixth addition of water. With further adsorbate, conduction dispersion has masked the effect. The observations again serve to emphasize the necessity for measurements at very high frequencies, and at lower temperatures. Silica gel and water appear to be an inconvenient system for study at lower temperatures. An isotherm at $-30°$ C. was abandoned because of the long time lags and the finding that the initial part of the first linear section was identical with the corresponding section at higher temperatures.

Results with Ethyl Chloride

Three isotherms were measured at +30°, 0°, and −30° C. The electrical measurements were made at frequencies up to 3.7 Mc. per sec. No Debye-type dispersion was noted even at the lowest temperatures. The data obtained were sufficiently similar to those reported earlier (6) that it is not necessary to quote them here. Again, assigning the normal liquid state value of the density at each temperature, a temperature coefficient of the molar polarization was observed along the first linear region, while a negligible temperature coefficient was observed along the second linear region.

In view of the formulae due to Kurbatov (4) and ourselves (7), the ethyl chloride adsorbed over the pressure range where the dielectric data reveal a temperature coefficient may be considered as a rotating dipole within a given cone angle or given angle of arc. The value of this angle, Ω^0, is 98°, whether the motion is considered possible in three dimensions, or is restricted to the adsorbent plane.

Along the second linear region the adsorbate must be considered to oscillate. The value of β^2 deduced by the Kurbatov formula is 4.8, which results in a value of the energy of 2800 cal. per mole. The value of β^2 deduced on the assumption of oscillations constrained to a plane is 0.84, and the value of the energy is 490 cal. per mole.

Ethyl Chloride – Water Results

Four isotherms were determined at 0.1° C. with the quantity of water in the gel varying from 0 to 250 cc. expressed as gas at N.T.P. The data are shown in Fig. 3 as plots of ΔC vs. volume of ethyl chloride adsorbed. It was found that the same initial and final slopes were obtained except at the highest moisture content, where even the first addition of ethyl chloride results in a lower value of the capacitance increment than found on dry silica. The position of the discontinuity of slope, obtained from the intersection of the linear sections, shifted progressively to lower quantities of ethyl chloride adsorbed. The shift of this position was not linear in the quantity of water adsorbed. It became less dependent on this quantity as the water content was increased.

To account for the observations an analysis based on an assumption of two types of adsorption site has been employed. It was postulated that both ethyl chloride and water are adsorbed on these two types of sites, and that for each site the polarizability of the molecule is characteristic. Since the experimental observations, both for water and ethyl chloride, showed a slight but regular change in the slope of formula (*a*) (Reference (6)) for each addition of adsorbate, it was possible to compute the fraction of each addition of adsorbate associated with the respective types of sites. (The trend in slope, although observable and quite regular if sufficient significant figures are employed, does not invalidate the assertion that linear sections of the plots exist to the precision with which the results have been given in tables and figures of this and other publications.) The computation of the fraction associated with each type of site also involves the assumption that the polarization may be accounted for as the sum of the polarizations associated with each type of site

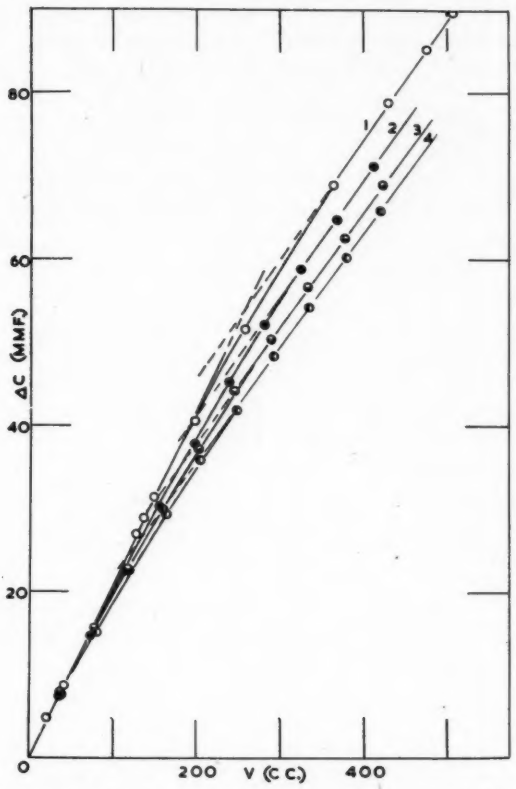

FIG. 3. Dielectric data for ethyl chloride and water systems at 0.1° C.

multiplied by the volume fraction of each addition adsorbed on each type of site.

Using the results obtained for the adsorbates separately, a calculation was made of the amount of ethyl chloride and water which would adsorb on each type of site as a function of the total amount adsorbed. These values were then applied to the isotherms for ethyl chloride on gel of varying water content. The results are given in Table I and it can be seen that the total volume ad-

TABLE I

H_2O content of gel, cc. at N.T.P.	H_2O adsorbed on Type I, cc. at N.T.P.	C_2H_5Cl adsorbed on Type I, cc. at N.T.P.	Total adsorbed on Type I, cc. at N.T.P.
Nil	Nil	234	234
85	79	155	234
175	140	101	241
250	180	71	251

sorbed on one of the types of site remains substantially constant, although the comparative quantities of water and ethyl chloride are quite different. Here the amount of water on Type I is calculated from the electrical data for water alone, while the value for ethyl chloride was obtained with the dry gel. The approximate constancy of the figures of the final column suggests that the treatment is a fair approximation.

To attempt to confirm this rationalization, the total volume adsorbed was considered to be given by an equation of the Langmuir form for two types of sites, that is

$$V = \frac{b_1 V_1 p}{1 + b_1 p} + \frac{b_2 V_2 p}{1 + b_2 p}.$$

The appropriate values of V_1 and V_2 for an isotherm at a given value of water content were then obtained by taking 234 cc. and subtracting the amount of

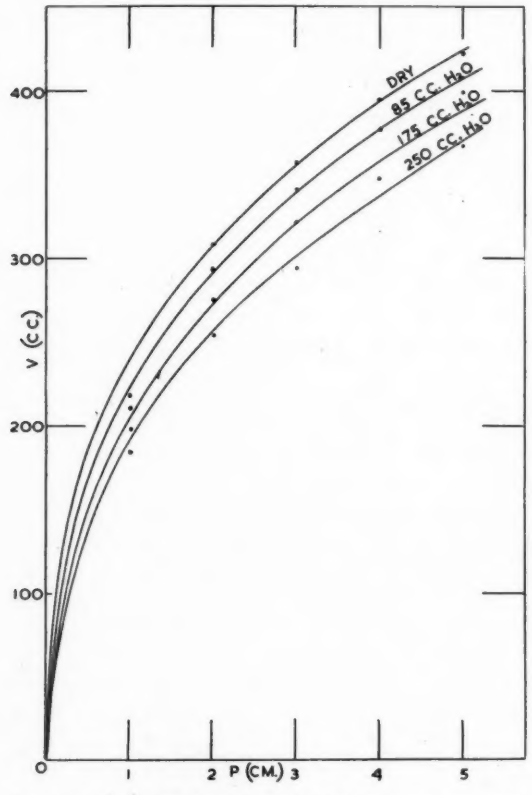

FIG. 4. Adsorption data of ethyl chloride – water systems.
Curves represent experimental values.
Points represent calculated values.

water on Type I sites, and by taking 466 cc., a value obtained from the saturation value for ethyl chloride on the dry gel in conjunction with the quantity on Type I sites, and subtracting the amount of water on Type II sites. From the isotherm for the dry gel b_1 and b_2 were evaluated, and these values were then employed for the isotherms of wet gels. The approximate agreement of theory and experiment is indicated in Fig. 4. The treatment is approximate, but serves to show that the electrical results for ethyl chloride in the presence of adsorbed water are semiquantitatively accounted for on the postulate that water and ethyl chloride are adsorbed on the same types of sites. The assumption of two types of sites appears sufficient to account for the nature of the observations.

The adsorption data for ethyl chloride, both on dry and wet gel, show the best agreement with theory when the Bradley–De Boer–Palmer equation is employed. This form of adsorption isotherm has been shown by Tompkins (8) to arise when nonlocalized monolayers are established on a surface with sites of a wide range of energies. This description of the system is inconsistent with the two site theory outlined above, but offers another possible explanation for the gradual change of polarization of the adsorbate with increasing surface concentration.

The slopes of the plots of the Bradley–De Boer–Palmer equation are independent of moisture content of the gel. Since the slope is related to the width of the distribution curve of the sites of various energies, and to the volume required to complete the unimolecular layer, it follows that the water must be distributed on the numerous types of sites in the same way as the ethyl chloride.

Butane and Water Mixtures

The adsorbates butane and water were studied in the same way as ethyl chloride and water at 0.1° C. The results, which are given in Table II and

TABLE II

DIELECTRIC DATA FOR BUTANE ON SILICA AT 0.1° C.

Water content of gel, cc. at N.T.P.	Dielectric constant using formula (a)		Refractive index squared
	First linear section	Second linear section	
Nil	1.79	1.74	1.81
44.6	1.74	1.72	1.81
89.1	1.74	1.70	1.81
167	1.70	1.68	1.81
361	1.70	1.62	1.81

represented graphically in Figs. 5 and 6, are very different. In the butane–water system the slope of the initial part of the ΔC vs. volume adsorbed plot did not change with increased moisture content. Moreover, beyond a moisture content of 167 cc. of water (as vapor at N.T.P.), there was no further change in the position of the intersection of the two linear sections of the plot, although

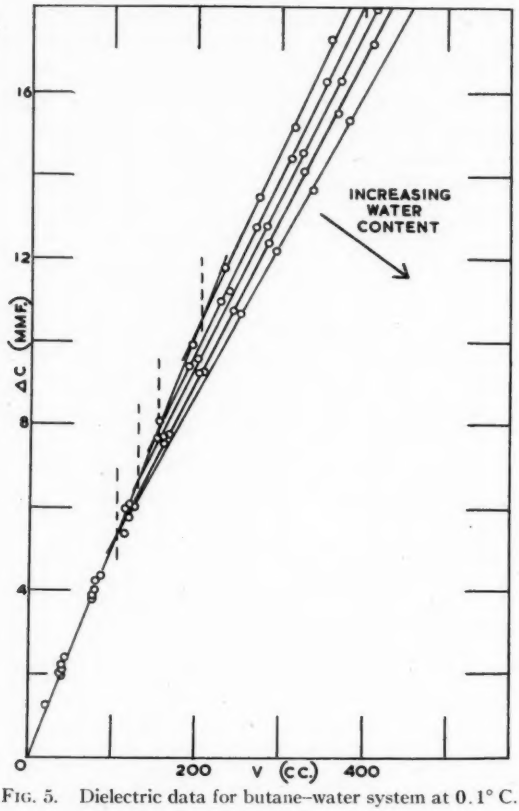

FIG. 5. Dielectric data for butane–water system at 0.1° C.

the isotherm is altered as shown in Fig. 6.

As can be seen from Table II, there is a variation of the apparent dielectric constant of the adsorbed material with moisture content for both sections of the data. In view of earlier discussions concerning nonpolar adsorbates (6), it appears necessary to explain the observed change in terms of a density variation. In this case it appears that the adsorbed film changes density to a limiting value along the first section, but that the value continues to alter along the second section. Such a view leads to speculation concerning the arrangement of the water and butane molecules in the adsorbent gel. With the present information, however, we have been unable to develop any self-consistent theory, particularly in view of the two facts that ethyl chloride and water appear to compete for the same sites, and that the isotherm continues to alter with increasing water content of the gel, while the electrical data over the range of low butane adsorption remain unaltered. It should be pointed out also that the butane–water data do not conform with the Bradley–De Boer–Palmer equation.

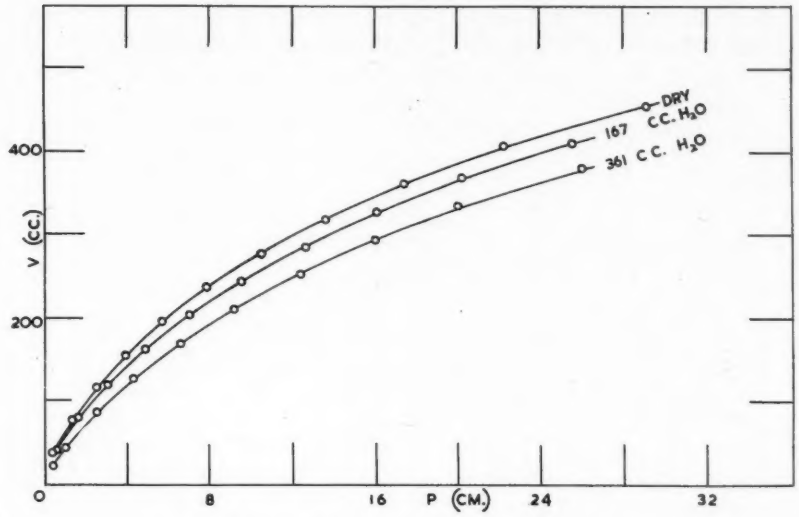

FIG. 6. Adsorption data for butane–water system at 0.1° C.

Clearly, such information must eventually be related with the abrupt change of apparent dielectric properties which has now been firmly established for a variety of systems, and concerning which no adequate comprehension can be claimed.

ACKNOWLEDGMENT

We are indebted to Prof. R. H. McKay of the Physics Department for valuable discussions and advice.

Grateful acknowledgment is made to the National Research Council for a grant in aid of this research and for a Studentship and Fellowship awarded to J. A. Snelgrove, and to the Advisory Committee on Research, University of Toronto, for financial support.

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THE ORIENTATIONAL POLARIZATION OF ADSORBED POLAR MOLECULES[1]

By J. A. Snelgrove[2] and R. McIntosh[3]

ABSTRACT

The orientational polarization of a polar molecule adsorbed on a solid surface is deduced for two cases. First, the molecule oscillates in the plane of the surface about some equilibrium position. A zero temperature coefficient of the polarization is deduced. Second, the molecule may rotate freely in the plane within some given angle, but cannot incline to any greater extent from the equilibrium position under the influence of the field. The normal temperature coefficient is obtained with this model.

The derivation of these formulae is based upon the procedures of Kurbatov who considered oscillation and rotation to be possible in three dimensions. The models employed here are considered preferable on the grounds that a physically adsorbed polyatomic molecule would presumably lie flat in the plane of the adsorbing surface.

INTRODUCTION

Recently Kurbatov (3) has derived several formulae for the orientational polarization of adsorbed polar molecules. He has treated two cases: one, a dipolar molecule which is attached to the surface at one end, and which may oscillate in three dimensions about some mean position in space; two, the dipolar molecule may rotate freely within a given cone angle, but cannot pass beyond the limits of the particular cone. Both these models would appear to be of value in explaining the observed behavior of adsorbed polar molecules. The first leads to the conclusion that a contribution to the over-all polarization from the orientational polarization may exist although a zero temperature coefficient of the polarization is also found. This is quite distinct from the case of a freely rotating dipole.

The second model leads to an expression for the orientational polarization which contains the absolute temperature in the same form as the Debye formula (2). The normal temperature coefficient has also been shown to result in the case of a dipolar molecule which may rotate freely in the plane of the adsorbing surface (4). The rotating dipole may be treated more generally in the manner developed by Kurbatov, and the angle on the plane, within which the molecule may rotate freely, may be deduced. The formula involved is identical with that given by Kurbatov, and no deduction of this particular case need be given.

It is also possible to consider the case of a polar molecule which is constrained to oscillate in the plane of the adsorbing surface. The result is somewhat different from that given by Kurbatov. The zero or negligible temperature coefficient of polarization is again deduced, but quite different values of the restoring energy are derived using the formula. Thus, the assumption of oscillations in three

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont. Taken from a thesis presented in partial fulfillment of the requirements for the Ph.D. degree of the Graduate School, University of Toronto.

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dimensions may lead to an energy term for the oscillator of 5000 cal. per mole (5), whereas oscillation in a plane with an energy of 500 cal. per mole results in the same value of the orientational polarization.

In view of the considerations stressed by DeBoer (1), and because of the general experimental evidence through heat of adsorption, it seems reasonable to expect that polyatomic molecules, which are physically adsorbed, will lie in the plane of the adsorbing surface. On this basis, the formula derived below is to be preferred to that given by Kurbatov.

Because of the intrinsic interest of the model and because the work of Kurbatov is not readily available in the English language, the development of the formula is given quite fully. It follows closely the procedure employed by Kurbatov, and the symbols employed are, where possible, the same as those used by him.

ORIENTATIONAL POLARIZATION OF A DIPOLE CONSTRAINED TO OSCILLATE IN A PLANE

Consider an adsorbed dipole μ which can execute small rotational oscillations of angular frequency ω about an equilibrium position in a plane. The oscillations are assumed to be simple harmonic. The particular plane considered has a given orientation, but for the system as a whole the planes are assumed to be orientated randomly. If, on application of a field F, the dipole oscillates about a new equilibrium position inclined with respect to the original position, the potential energy of the dipole will be altered. The change of potential energy arises from the displacement to the new equilibrium position and the force of attraction to the former equilibrium position, and from the inclination in the new equilibrium position with respect to the applied field. Hence, following Kurbatov and employing Boltzmann statistics, the probability of the dipole having a new equilibrium orientation between Ω and $\Omega + d\Omega$ with respect to the position when no field is acting is proportional to

$$e^{-\beta^2\Omega^2} e^{(\mu F \cos x)/kT} d\Omega$$

for small values of Ω. Here, $\beta^2 = \omega^2 I/2kT$, where I is the moment of inertia of the dipole with respect to the axis of rotation, and k is the Boltzmann constant per molecule. Here $\mu \cos x$ gives the component of the dipole in the direction of the field, which is taken to be along the x axis. The relation among $\cos x$, Ω, and the orientation of the plane is given by

$$\cos x = \cos \psi \cos \theta \cos \Omega + \sin \theta \sin \Omega.$$

The position of the normal line to this particular plane is defined by the angles θ and ψ with the coordinate axes, ψ being the azimuthal angle.

The probability of the dipole being within the angle between Ω and $\Omega + d\Omega$ is thus proportional to $e^{-\beta^2\Omega^2} e^{\alpha \cos x} d\Omega$, where α is $\mu F/kT$. The total moment of such dipoles in the direction of the field for all values of Ω is

$$A \int_0^{2\pi} e^{-\beta^2\Omega^2} e^{\alpha \cos x} \mu \cos x \, d\Omega,$$

where A is a constant depending upon the number of dipoles. The mean value

of the projection of the moment in the direction of the field for such dipoles in the plane, the orientation of which is given by θ, ψ, is

$$(a) \qquad \bar{m}_{\theta,\psi} = \frac{A\int_0^{2\pi} e^{-\beta^2\Omega^2} e^{\alpha\cos x}\,\mu\cos x\,d\Omega}{A\int_0^{2\pi} e^{-\beta^2\Omega^2} e^{\alpha\cos x}\,d\Omega}.$$

The integrals may be evaluated by a procedure which is illustrated by using the numerator. Where $\alpha \ll 1$, that is for weak fields, the exponential term involving α may be expanded in a series and only the first two terms retained. The numerator then becomes

$$\int_0^{2\pi} e^{-\beta^2\Omega^2}(1+\alpha\cos\psi\cos\theta\cos\Omega)(1+\alpha\sin\theta\sin\Omega) \times (\mu\cos\psi\cos\theta\cos\Omega+\mu\sin\theta\sin\Omega)d\Omega.$$

Neglecting terms in α^2 and rewriting as constants the terms not involving Ω, we have

$$(b) \qquad \int_0^{2\pi} e^{-\beta^2\Omega^2}(1+k_1\cos\Omega+k_2\sin\Omega)(k_3\cos\Omega+k_4\sin\Omega)d\Omega$$

where $\alpha\cos\psi\cos\theta = k_1$, $\alpha\sin\theta = k_2$, $\mu\cos\psi\cos\theta = k_3$, and $\mu\sin\theta = k_4$. The integral may be evaluated term by term. First extend the upper limit to infinity. This introduces no serious error for values of $\beta^2 \geqslant 0.1$, that is, for sufficiently rigid binding of the dipole, owing to the rapid convergence of the functions being integrated. A graphical test of this statement was made for $\beta^2 = 0.1$, and the areas arising in each term are less than 1% of the area for the appropriate term up to the limit 2π. A method of evaluating the integrals is as follows

$$e^{-\beta^2\Omega^2+i\Omega} = e^{-\beta^2\Omega^2}(\cos\Omega + i\sin\Omega).$$

The real part is $e^{-\beta^2\Omega^2}\cos\Omega$ and the imaginary part is $ie^{-\beta^2\Omega^2}\sin\Omega$.

Now let $z = \beta\Omega - i/2\beta$ and

$$\int_0^\infty e^{-\beta^2\Omega^2+i\Omega}\,d\Omega = \frac{1}{\beta}e^{-1/4\beta^2}\int_0^\infty e^{-z^2}\,dz + \frac{1}{\beta}e^{-1/4\beta^2}\int_{-i/2\beta}^0 e^{-z^2}\,dz.$$

Hence $\int_0^\infty e^{-\beta^2\Omega^2}\cos\Omega\,d\Omega$ is given by the real part of the above equation, while $i\int_0^\infty e^{-\beta^2\Omega^2}\sin\Omega\,d\Omega$ is given by the imaginary part. To deal with the imaginary part the substitution $z = iv$ is made, and the integral becomes

$$i\frac{1}{\beta}e^{-1/4\beta^2}\int_0^{1/2\beta} e^{v^2}\,dv.$$

Here the exponential is expanded and the first two terms of the series are retained.

By employing these procedures and evaluating each term in (*b*), one obtains for the numerator of (*a*)

$$\frac{k_3\sqrt{\pi}}{2\beta}\,e^{-1/4\beta^2}+k_4e^{-1/4\beta^2}\left(\frac{1}{2\beta^2}+\frac{1}{24\beta^4}\right)+\frac{k_1k_3\sqrt{\pi}}{4\beta}\left(1+e^{-1/\beta^2}\right)$$
$$+\frac{k_2k_4\sqrt{\pi}}{4\beta}\left(1-e^{-1/\beta^2}\right)+\frac{k_2k_3+k_1k_4}{2}\,e^{-1/\beta^2}\left(\frac{1}{\beta^2}+\frac{1}{3\beta^4}\right).$$

The denominator becomes

$$\frac{\sqrt{\pi}}{2\beta}+\frac{k_1\sqrt{\pi}}{2\beta}\,e^{-1/4\beta^2}+k_2e^{-1/4\beta^2}\left(\frac{1}{2\beta^2}+\frac{1}{24\beta^4}\right).$$

Now let

$$\frac{\sqrt{\pi}}{2}\,e^{-1/4\beta^2}=k_5,\quad e^{-1/4\beta^2}\left(\frac{1}{2\beta}+\frac{1}{24\beta^3}\right)=k_6,\quad \frac{\sqrt{\pi}}{4}\left(1+e^{-1/\beta^2}\right)=k_7,$$
$$\frac{\sqrt{\pi}}{4}\left(1-e^{-1/\beta^2}\right)=k_8,\quad \frac{1}{2}\,e^{-1/\beta^2}\left(\frac{1}{\beta}+\frac{1}{3\beta^3}\right)=k_9,\quad \frac{\sqrt{\pi}}{2}=k_{10}.$$

Then $\bar{m}_{\theta,\psi}$ becomes

$$(c)\qquad \frac{k_5\,\mu\cos\psi\cos\theta+k_6\,\mu\sin\theta+k_7\,\alpha\mu\cos^2\psi\cos^2\theta+k_8\,\alpha\mu\sin^2\theta}{k_{10}+k_5\,\alpha\cos\psi\cos\theta+k_6\,\alpha\sin\theta}$$
$$+\frac{2k_9\,\alpha\mu\cos\psi\cos\theta\sin\theta}{k_{10}+k_5\,\alpha\cos\psi\cos\theta+k_6\,\alpha\sin\theta}.$$

To evaluate $\bar{m}$, the mean value of the component of the dipole in the direction of the field, on the assumption of uniform adsorption density, the averaging process is given by

$$(d)\qquad \bar{m}=\frac{\int_0^{\pi}\int_0^{2\pi}\bar{m}_{\theta,\psi}\sin\psi\,d\theta\,d\psi}{\int_0^{\pi}\int_0^{2\pi}\sin\psi\,d\theta\,d\psi}.$$

The exact integration of all the terms in (d) arising through $\bar{m}_{\theta,\psi}$ is not possible but if we use the first two terms of the binomial expansion of the denominator in (c), the equation

$$\bar{m}_{\theta,\psi}=\frac{1}{k_{10}}\Big(k_5\,\mu\cos\psi\cos\theta+k_6\,\mu\sin\theta+k_7\,\alpha\mu\cos^2\psi\cos^2\theta+k_8\,\alpha\mu\sin^2\theta$$
$$+2k_9\alpha\mu\cos\psi\cos\theta\sin\theta\Big)\left(1-\frac{k_5}{k_{10}}\alpha\cos\psi\cos\theta-\frac{k_6}{k_{10}}\alpha\sin\theta\right)$$

results. Again terms in α^2 are neglected and the integral is evaluated term by term. Finally, there is obtained

$$(e)\qquad \bar{m}=\frac{\alpha\mu}{3}\left(1-\frac{1}{2}\,e^{-1/\beta^2}-\frac{1}{2}\,e^{-1/2\beta^2}-6\,e^{-1/2\beta^2}\left(\frac{1}{2\beta}+\frac{1}{24\beta^3}\right)^2\Big/\pi\right).$$

In the limits when $\beta^2=0$ (free rotation) and $\beta^2=\infty$ (rigid binding), this reduces as expected to

$$\bar{m}=\frac{\alpha\mu}{3}\text{ and }\bar{m}=0,\text{ respectively.}$$

When the first two exponential terms of equation (*e*) are expanded into a series and the first two terms are retained,

$$\bar{m} = \frac{\alpha\mu}{3}\,\frac{3}{4\beta^2} = \frac{\mu^2 F}{2\omega^2 I}.$$

The contribution of the orientational component to the total polarization is

$$P_\mu = \frac{2\pi N}{3}\,\frac{\mu^2}{\omega^2 I} \qquad (f)$$

which is independent of temperature. This result is to be compared with that obtained by Kurbatov where oscillation is possible in three dimensions, namely

$$\frac{8\pi N}{9}\,\frac{\mu^2}{\omega^2 I}. \qquad (g)$$

It should be noted that the lack of a temperature term is rigorous only for reasonably large values of β^2. With β^2 as small as 0.1 the polarization, as calculated from equation (*e*), is less at 350° A. by about 10% than that at 300° A., while if the Debye form of the equation were involved, the reduction would be about 15%. With $\beta^2 = 0.2$ there is virtually no change of the orientational polarization for such a temperature change.

For any given temperature the orientational polarization may be conveniently expressed by means of the Debye term and a correction factor designated as a by Kurbatov, that is,

$$\bar{m} = \frac{a\mu^2 F}{3kT}.$$

The correction factor varies from a value of one when $\beta^2 = 0$, to zero when $\beta^2 = \infty$. In Fig. 1 are shown the values of a as a function of β^2 for oscillation in three dimensions, and for oscillation restricted to a plane. The value of a for the oscillator in the plane (curve 2) lies below that for the model treated by

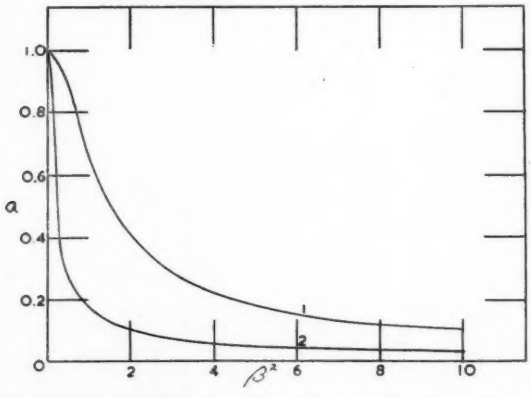

FIG. 1. Correction factors to Debye term for oscillating dipoles as a function of β^2.

Kurbatov (curve 1). This leads to values of β^2 which are much less for the oscillations in the plane than for the model examined by Kurbatov at any given measured value of the orientational polarization. Cases in point have been presented for several adsorbates on activated silica (5).

FREE ROTATION WITHIN A GIVEN ANGLE ON A PLANE

The orientational polarization of a dipolar molecule which can rotate freely within a given angle on the adsorbing plane, but which cannot rotate beyond this angle, may be developed by a similar modification of Kurbatov's treatment. The necessary relations are:

$$(h) \qquad \bar{m}_{\theta,\psi} = \frac{A\int_0^{\Omega^\circ} e^{\alpha \cos x}\,\mu \cos x\, d\Omega}{A\int_0^{\Omega^\circ} e^{\alpha \cos x}\, d\Omega}$$

$$(i) \quad \text{and} \qquad 4\pi\bar{m} = \int_0^{2\pi}\int_0^{\pi} \bar{m}_{\theta,\psi} \sin\psi\, d\psi\, d\theta.$$

The formula deduced is the same as that given by Kurbatov, namely,

$$(j) \qquad \bar{m} = \frac{\mu^2 F}{3kT}\left(1 - \cos^4\frac{\Omega^0}{2}\right)$$

where Ω^0 is the limiting inclination of the dipole on either side of its equilibrium position in the plane. The correction factor to the Debye term, designated by the symbol a_1, is shown as a function of the angle Ω^0 in Fig. 2. It may be noted

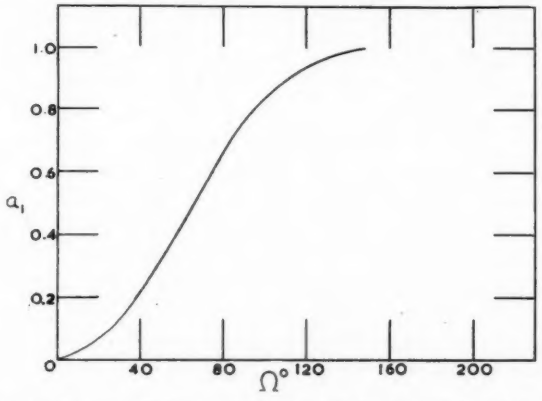

Fig. 2. Correction factor to Debye term for rotating dipoles as a function of limiting angle for free rotation Ω^0.

that for rotation through an angle of 180°, the correction factor is one, in agreement with the result given by McIntosh, Rideal, and Snelgrove (4) for free rotation on a plane. Furthermore, it is seen that the normal temperature coefficient is predicted.

CONCLUSIONS

On the basis of these formulae it is possible to interpret the experimental observations of the polarization of adsorbed molecules as arising either from oscillating dipoles or from freely rotating dipoles within some given angle of permitted rotation. In the former case no temperature coefficient is to be expected; in the latter, the normal temperature variation will be observed. It must be remembered, however, that values of the restoring energy or of the angle within which free rotation is possible both depend upon the absolute value of the total polarization which is computed from the experimental results. The absolute value of this quantity depends upon an arbitrary assignment of the density of the adsorbed phase. The uncertainty in this factor can only be eliminated by a determination of the polarization at such high frequencies that any contribution from orientational polarization is negligible.

ACKNOWLEDGMENT

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THE DECOMPOSITION OF SOLID POTASSIUM PERCHLORATE BY 50 KILOVOLT X RAYS[1]

By H. G. Heal[2]

ABSTRACT

Potassium perchlorate crystals are decomposed by 50 kv. X rays. The main products of the primary decomposition are chlorate and chloride, but small amounts of unidentified oxidizing substances are also formed. The chlorate decomposes by a secondary reaction to chloride. These reactions are approximately of the first order. The average amount of X-ray energy absorbed by the salt per ClO_4^- ion decomposed is 19 ± 2 ev.

INTRODUCTION

In recent years interest in the decomposition of solid salts by ionizing radiation has been stimulated by the increasing use of the Szilard–Chalmers method for separating radioisotopes. This method makes use of the change in the state of chemical combination of atoms, caused by the recoil accompanying an (n,γ) reaction, to separate these atoms from the bulk of the material. Solid salts containing complex ions, e.g. permanganates, chromates, and perchlorates, have given excellent results in Szilard–Chalmers separations. When the samples are irradiated in a nuclear reactor, however, the Szilard–Chalmers effect is often accompanied by partial decomposition of the nonradioactive bulk of the salt. This is due in the main to γ rays, which are, of course, unavoidably present at high intensities. It can seriously impede the separation of the radioactive isotope that is sought.

It is now being recognized that such decompositions, although a nuisance from the technical standpoint, are actually quite interesting problems in their own right. Burton in 1947 (3) pointed out the need for more work in this neglected field. The present paper describes an investigation with the object of finding out something about the mechanism of a typical decomposition of this kind. This work differs from most previous researches in the field in having as its principal aims the study of the reaction kinetics and energy utilization.

Newton (8) observed, but did not investigate in detail, the decomposition occurring when potassium chlorate or perchlorate is irradiated in a nuclear reactor for the separation of Cl^{36} by the Szilard–Chalmers effect. The decomposition of potassium bromate associated with Szilard–Chalmers separation of Br^{82} has also been studied (2). It is appropriate to mention, in addition, the work of Günther, Lepin, and Andreev (6) on the X-ray decomposition of barium azide, that of Allen and Ghormley on the decomposition of barium nitrate by Van de Graaff electrons (1), and that of Müller and Brous (7) on the decomposition of sodium azide by slow electrons.

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Contribution from Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ont. Issued as A.E.C.L. No. 17.
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EXPERIMENTAL METHODS

Irradiations in a nuclear reactor suffer from the drawback of mixing several kinds of radiation effects, and the energy absorbed cannot be measured easily. Low-voltage beryllium-windowed X-ray tubes provide a means of administer-

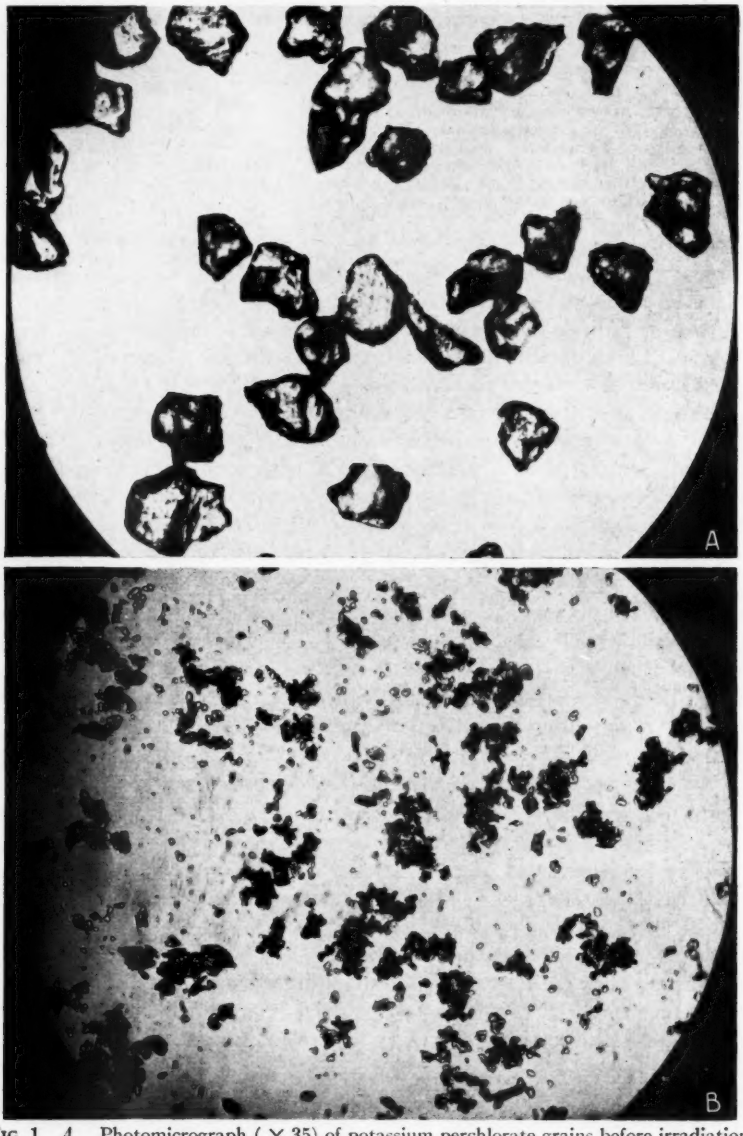

FIG. 1 *A*. Photomicrograph (× 35) of potassium perchlorate grains before irradiation.
B. $KClO_4$ grains (× 35) after 60 hr. irradiation.

ing doses of radiation comparable with those obtainable in such a reactor, but consisting only of one kind of radiation. They can be operated with light shielding, and in a manner permitting of accurate dosage measurement. In this investigation a Machlett AEG-50-T tube with tungsten target, beryllium window, and 5 mm. focal spot was employed. It was run at 50 kvp., 50 ma., using full-wave rectified but unfiltered high-voltage. The voltage and milliamperage were maintained within 2% of these values during the irradiation by manual adjustment.

Preparation of Potassium Perchlorate Samples

Reagent grade potassium perchlorate was recrystallized several times from double distilled water. It was ground and sifted through 200- and 325-mesh screens, the grains which fell between these two sizes being selected for the irradiation. In this way grains within an average diameter of about 0.1 mm., and fairly uniform in size (as Fig. 1*A* shows), were obtained. Uniform grains were required because of the possibility that the course of the reaction might depend on the grain size. Samples of this material averaging 1 mgm. were weighed by a semimicro balance sensitive to 0.01 mgm., into the irradiation cell shown in Fig. 2*B*. This was made from two ½-in. square microscope cover

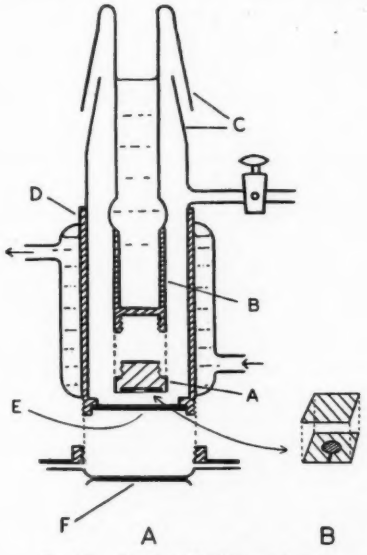

FIG. 2. *A*. Irradiation equipment.
B. Irradiation cell.

glasses. One, about 0.2 mm. thick, had a circular depression of 5 mm. diameter etched in its center by hydrofluoric acid, with a fine channel leading from this depression to the edge of the glass, to permit free passage of gases. The sample was spread out over the bottom of this depression with a microspatula. The other cover glass, 0.1 mm. thick, was then placed over the sample. In this way

the salt was held in place in a layer one grain thick. This arrangement was required to guarantee reproducible conditions of irradiation, and also to prevent scattering of the grains of salt in the decrepitation which occurs during irradiation. The whole "sandwich" was fastened with a clip of steel wire to the under side of the copper block, (*A*) in Fig. 2*A*, which was screwed into the thimble *B*. The 0.1 mm. thick cover glass faced the X-ray tube.

A few larger samples, about 5 mgm., were used for the qualitative identification of products. These were also irradiated in a thin layer between two cover glasses.

Procedure in Irradiations

The ground joint *C* (Fig. 2*A*) was greased with Apiezon *L* and connected. The vessel was evacuated to 0.0001 mm. pressure, and then filled with purified helium (99.99% He) at a pressure between 0.3 and 0.7 atmosphere. This was mainly for the purpose of conducting heat away from the sample during irradiations. Actually, rough calculations later carried out to determine the rate of heat loss from the salt by radiation suggest that this precaution was unnecessary: it seemed that even in a high vacuum the temperature of the salt could hardly rise more than about 2° above that of the surroundings. It was shown that with other conditions equal, the yields of chloride and chlorate obtained in typical irradiations of potassium perchlorate did not alter significantly when a high vacuum was substituted for the helium atmosphere during irradiation. The brass jacket (*D*) and inner thimble (*B*) of Fig. 2*A* were kept at 25° throughout the irradiations by circulating water. The distance between the sample and the window *F* of the X-ray tube was about 1 cm. The axis of the thimble (*B*) passed through the centers of the sample and the X-ray tube window. *E* in Fig. 2*B* is a 1 mm.-thick beryllium window soldered in a monel ring, which is soldered to the brass casing *D*. The glass to metal joint is made with vacuum wax.

Analytical Methods

The irradiated potassium perchlorate was analyzed for chloride, chlorate, and other oxidizing agents. Chloride was determined by titration with silver nitrate. Chlorate was measured by means of its ability to oxidize ferrous ion in hot acid solution, and other oxidizing agents by the oxidation of ferrous ion in the cold. Perchlorate does not oxidize ferrous ion in solution under any conditions.

The various substances described here as "other oxidizing agents" were not fully identified. The total amount of these was always small compared with the amounts of chloride and chlorate. Absorption spectra of the solutions suggested that chlorite and hypochlorite ions were present.

A typical sample was analyzed as follows. The irradiated salt was washed with a few drops of water into a 5 ml. beaker, and the solution weighed. After the solution had been mixed, an aliquot, usually 0.2 ml., was taken by means of a micropipette and added directly to an excess of 14 m*M* ferrous sulphate in 0.8 *N* sulphuric acid, to which a drop of 2 *N* sulphuric acid had been

added. The solution was left to stand a minute or two. Then 0.5 ml. of saturated *o*-phenanthroline solution and 1 ml. of 2 *M* sodium acetate were added. The volume was made up to 5 ml., and the color intensity measured with a Klett–Summerson photoelectric colorimeter, using a green filter. This gave the total number of equivalents of all oxidizing agents except chlorate, which does not oxidize ferrous ion under these conditions. For the determination of chlorate, another aliquot, generally 0.02 ml., was added to 0.05 ml. of the same acid ferrous solution in a short piece of 7 mm. diameter glass tubing sealed at one end. This was then drawn out in a flame and sealed off. A similar capsule containing only the ferrous solution was prepared to serve as a blank. The two were immersed in boiling water for an hour. They were then cut open. The contents were washed out and analyzed for residual ferrous ion as described above. This gave the total equivalents of all oxidizing agents including chlorate, from which the chlorate was determined by difference. Air oxidation of the blank was appreciable but not serious, while the reduction of chlorate was not quite complete. A correction, amounting to 8%, which had been determined with the aid of standard chlorate samples, was added to all results to compensate for incompleteness of reduction of chlorate ion.

Chloride was determined on the portion of the original solution remaining after withdrawal of these aliquots. It was transferred by pipette, together with washings, to a 1 ml. beaker, and evaporated down to about 0.2 ml. under an infrared lamp. The solution was titrated with 0.025 *M* silver nitrate from a microburette. The end point was determined electrometrically. One electrode was a piece of silver wire. The other was a platinum wire dipping into dilute potassium nitrate solution in a small vessel which communicated by a fine capillary with the titration vessel. This probably functioned as an oxygen electrode, and maintained a satisfactorily constant potential during titrations. The e.m.f. was measured with a vacuum tube voltmeter (Beckman pH meter). In order to eliminate any danger of the solution in the titration beaker flowing up into the tip of the burette and into the reference electrode, its density was increased by the addition of a drop of 16% pure potassium nitrate solution to each sample.

It was established by blank experiments that chloride and chlorate did not interfere with the chlorate determinations, nor chlorate and perchlorate with the chloride determinations.

Measurement of Energy Absorbed by the Sample

The shape of the energy spectrum of radiation emitted by the X-ray tube target was calculated by means of De Waard's formula (4). Only the continuous spectrum was considered, since the voltage applied to the tube was insufficient to excite the *K* lines of tungsten, and the intensities of the other lines are negligibly small. Fig. 3*A* shows I_λ plotted against the wave length. I_λ is a function such that the total energy flux in the wave length range λ to $\lambda + d\lambda$ is equal to $I_\lambda\, d\lambda$. The reduction in intensity due to absorption in the two beryllium windows and the cover glass was calculated for a series of wave lengths, using tabulated values of the mass absorption coefficients. For this

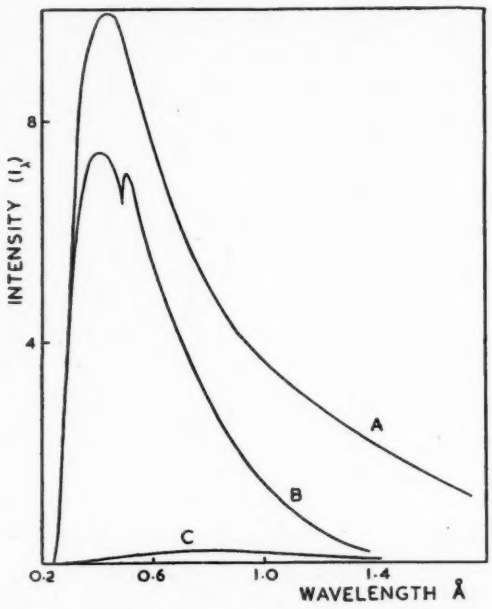

FIG. 3. *A*. Energy spectrum of X rays from tungsten target at 50 kv.
B. Spectrum of X rays striking the salt.
C. Spectrum representing energy absorbed in potassium perchlorate samples as a function of X-ray wave length.

purpose it was necessary to know the chemical composition of the cover glass. This information was kindly supplied by the makers. The shape of the "filtered" spectrum, as it impinged on the sample, is shown in Fig. 3*B*. By similar methods the fraction of the incident energy absorbed by the sample at a variety of wave lengths could then be calculated. Fig. 3*C* shows a function (of the same kind as I_λ) of the energy absorbed by the sample, plotted against wave length. The areas under 3*A* and 3*B* represent the relative total energy fluxes in the unfiltered and filtered beam respectively, while the area under 3*C* represents, in its correct proportion, the energy absorbed by the sample. Under the conditions of the experiments, wave lengths around 0.8 Å contribute most energy to the salt, although the peak in the total flux emitted by the tube comes at about 0.4 Å.

The total flux at the position of the sample was determined calorimetrically. The block *A* in Fig. 2*B* was removed and a silver disk 5 mm. in diameter and 0.5 mm. thick was placed in the exact position usually occupied by the sample, being supported by the leads of a copper–constantan thermocouple soldered to its back. The cold junction of the circuit was made by soldering the other end of the constantan lead to the thimble *B* of Fig. 2*B*. With the vessel highly evacuated, the e.m.f. developed by the thermocouple in the full X-ray beam was measured. It corresponded to a temperature rise in the silver disk of

nearly 6°C. The X-ray beam was switched off, and a cooling curve plotted. The cooling of the disk followed Newton's law of cooling within the error of measurement. The disk was detached and weighed. Knowing its mass and specific heat, it was possible to calculate the rate of heat loss by the disk at the equilibrium temperature reached by it in the X-ray beam, in calories per second. This was, of course, equal to the rate of energy input from the X-ray beam. Since the incident energy was for all practical purposes totally absorbed by the disk, the same figure gave the total energy flux in the beam, over a cross section equal to the area of the disk. With the aid of area measurements on the graphs of Fig. 3, it was then a simple matter to calculate the absolute rate of energy absorption in the sample. A possible objection to this method of calculation arises when the actual mechanism of energy absorption is more closely considered. The primary process by which an X-ray quantum is absorbed is the production of a photoelectron, which is actually the effective agent in ionizing and exciting the medium. The energy of a photoelectron corresponding to the peak wave length in Fig. 3*C* is in the region of 10 kv. to 20 kv., and the range of such an electron is of the order of 1 mgm. per cm.^{2} of aluminum, or rather less. Since the thickness of the sample is only about 5 mgm. per cm.^{2}, some photoelectrons must evidently escape from the surfaces of the sample without producing their full complement of ionization and excitation. For samples of this thickness, loss is of the order of 5% of the total energy absorbed by the sample. It must be remembered, however, that the sample is enclosed between glass plates which have roughly the same stopping power both for X rays and for electrons as the sample itself. This means that the loss of electrons from the surfaces of the sample is fairly exactly compensated by the entry of electrons from the glass plates into the sample.

The correctness of the absorption calculations was tested by substituting for the 0.1 mm. cover glass filter a cover glass of the same material but twice the thickness. The reduction in yield of Cl^- and ClO_3^- thereby caused was determined. The observed yield was smaller by a mean factor of 1.8 than previously, whereas the calculations predicted a reduction by a factor of 1.7. This agreement was considered adequate for an investigation not aiming at the highest accuracy.

RESULTS AND DISCUSSION

Potassium perchlorate darkens in color to golden brown in the first few minutes of irradiation. Thereafter the color changes but slowly. There is a tendency to lighten somewhat in very long irradiations. This color is presumably due to displaced and trapped electrons. In other respects the appearance of the grains remains unchanged up to four hours' irradiation at 50 kv., 50 ma. The grains then decrepitate and fall to a fine powder (Fig. 1*B*). The irradiated samples dissolve in water with effervescence, unless they have been irradiated for a very long time, when the effervescence becomes scarcely noticeable.

Kinetic and Energetic Features of the Decomposition

Fig. 4 represents the number of moles of ClO_3^-, Cl^-, and other products

(expressed as ClO_2^-) formed in one mole of $KClO_4$ during irradiation for periods up to 60 hr.

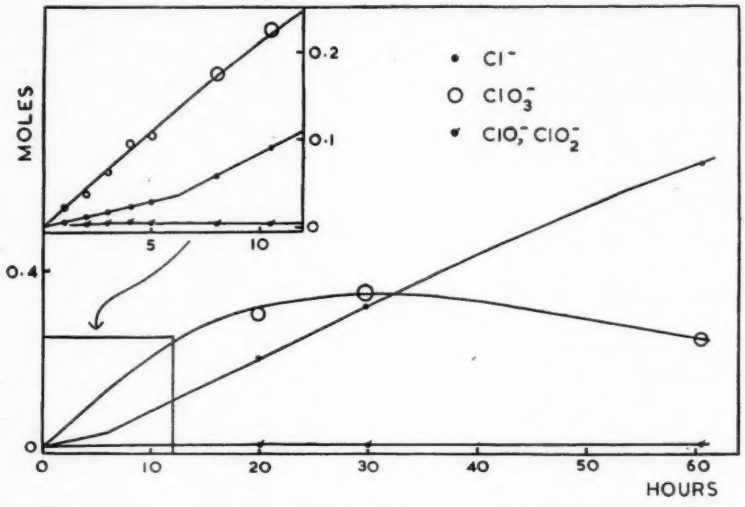

FIG. 4. Diagram showing the yields of chloride, chlorate, and other products obtained in irradiation of 1 mole of potassium perchlorate for various periods.
(*Insert*) A magnified portion of the main diagram, showing yields in the first 12 hr. irradiation. The size of the circles for chlorate ion represents the estimated possible analytical error. The analytical errors in the determination of chloride and other products are smaller than the size of the circles.

The following conclusions emerge from a study of Fig. 4:

(1) Cl^- and ClO_3^- are both formed directly from ClO_4^- under irradiation, at first in the ratio of about 1 mole to 4 moles. Cl^- is not formed solely as a secondary product resulting from the decomposition of ClO_3^- first formed, although it is probably formed by this mechanism also. These facts are shown by the formation of Cl^- at a constant rate at the very beginning of the irradiation. The rapid increase in the amount of ClO_3^- present during the first four hours does not apparently affect the rate of formation of Cl^-. In other words, at the beginning of irradiation, when the crystal lattice is substantially that of pure potassium perchlorate, the reactions

$$KClO_4 \rightarrow KClO_3 + \tfrac{1}{2}O_2,$$
$$KClO_4 \rightarrow KCl + 2O_2$$

proceed simultaneously, the first being about four times as likely as the second.

(2) There is a secondary decomposition of ClO_3^- to Cl^- and O_2. This is shown by the fact that the amount of ClO_3^- in the sample passes through a maximum and then decreases again as irradiation continues. It is noteworthy that this secondary decomposition of ClO_3^- does not give rise to significant amounts of ClO_2^- and ClO^-, although they do appear to be formed in quite

large amounts in the direct irradiation of potassium chlorate.* The only obvious explanation of this difference is the different physical state of the material in the two cases.

(3) About five hours after irradiation commences, the rate of Cl^- formation is suddenly approximately doubled, while the rate of formation of ClO_3^- does not change. This phenomenon occurs at the same time as the breakdown of the crystals of potassium perchlorate to a fine powder, and may therefore be connected with the increase of surface area or with the rearrangement of the crystal lattice.

Because of the break in the Cl^- curve (Fig. 4) it is clear that the kinetics of the reaction cannot be completely explained by any simple mechanism. The portion of the Cl^- curve before the break is, however, small compared with the whole curve, and as a first approximation can be neglected. If this is done, the following simple picture will explain roughly the shapes of the curves in Fig. 4. The decomposition of potassium perchlorate is approximately of the first order, with velocity constant (under the special conditions of these experiments) equal to 0.0371 $hr.^{-1}$ This velocity constant includes a contribution of 0.011 arising from the decomposition to Cl^-, whereas the rest, 0.0260, comes from decomposition to ClO_3^- (other modes of decomposition being neglected). Fig. 5 shows that the logarithm of the quantity of potassium perchlorate in

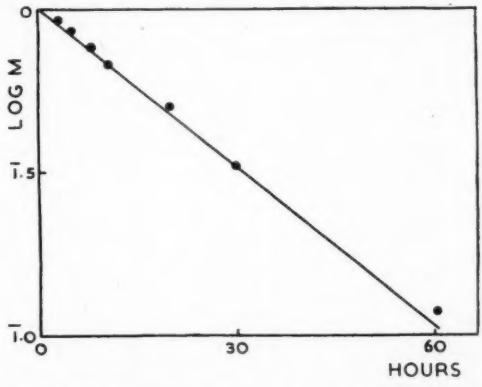

FIG. 5. Logarithm of the number of moles (M) of potassium perchlorate left undecomposed after various periods of irradiation of 1 mole potassium perchlorate.

the sample, when plotted against time, gives a good straight line, as required for a first order reaction. The ClO_3^- also decomposes by an approximately first order reaction to Cl^-. If a value for the velocity constant of this decompo-

* *In some preliminary experiments on the irradiation of crystalline potassium chlorate under the same conditions as the irradiation of potassium perchlorate described here, chloride, hypochlorite, and chlorite all appeared to be formed in comparable and continuously increasing amounts. The reaction products from this irradiation were tentatively identified by their absorption spectra in aqueous solution and by the reaction with silver nitrate, but the identification is not yet complete or altogether satisfying.*

sition equal to 0.0200 is adopted, the shape of the ClO_3^- curve is not badly described, and the same is true of the Cl^- curve (Fig. 6).

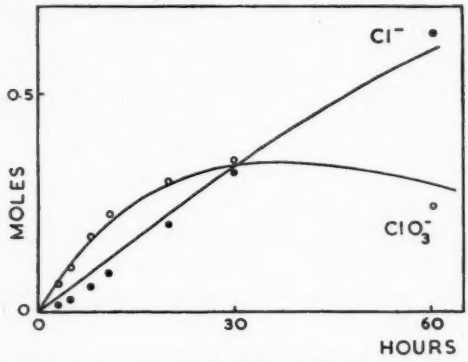

FIG. 6. The curves represent calculated yields of chlorate and chloride from irradiation of 1 mole potassium perchlorate for various periods, assuming first-order decomposition of ClO_4^- and ClO_3^-. The points represent experimentally determined yields.

By comparing the total number of ClO_4^- ions decomposed per unit time, during the first four hours of the reaction, with the rate of energy absorption determined calorimetrically, one obtains for the average energy required to decompose a ClO_4^- ion the figure of 19 ± 2 ev. This corresponds to 440 kcal. per mole $KClO_4$. ΔH for the reaction

$$KClO_4 \rightarrow KCl + 2O_2$$

is 7.9 kcal., while for the reaction

$$KClO_4 \rightarrow KClO_3 + \tfrac{1}{2}O_2$$

ΔH is 22.2 kcal. Therefore the over-all utilization of energy in the decomposition is quite inefficient. It is more legitimate to compare the energy required for the decomposition with that required to raise the perchlorate ion from the ground state to its first excited level, which is at least 5.4 ev.* The energy of activation for the decomposition may be greater than this, but cannot well be less, since electronic excitation or ionization of ClO_4^- is the only possible way in which decomposition can be initiated. Thus it follows that at least 30% of the energy absorbed is used in activating the decomposition. The figure of 19 ev. absorbed per molecule decomposed is of the same order as that found for radiation-induced reactions in gases and aqueous solutions.

The Mechanism of the Decomposition of Potassium Perchlorate

Photoelectrons resulting from the primary absorption process travel through the perchlorate lattice, where they may either split off electrons from ClO_4^- ions: —

$$ClO_4^- \rightarrow ClO_4 + e \qquad [1]$$

or excite ClO_4^- ions electronically without electron loss: —

$$ClO_4^- \rightarrow ClO_4^{-*}. \qquad [2]$$

* *This figure can be deduced from the fact that the ultraviolet absorption of the ClO_4^- ion in aqueous solution begins around 2300 Å. Exact figures for the wave lengths of absorption bands in solid potassium perchlorate do not seem to be available.*

Both processes presumably occur, and it becomes necessary to decide whether either or both leads to decomposition. The fact that ions found in the solution of irradiated salt cannot be assumed to be necessarily present in the solid adds to the difficulty of this problem.

Reaction [1] would give ClO_4, which is not now believed to exist as a chemical entity. It is difficult to account for the electrons which would be set free in this reaction, if it occurred. They could either be recaptured by ClO_4, with no net reaction, or trapped at lattice imperfections, giving rise to color centers. Since the color of the salt does not darken further after a very few minutes' irradiation, and is never very dark, there can be but small numbers of trapped electrons. Reaction [1] is therefore believed to contribute little, if at all, to the over-all decomposition, and reaction [2] must be accepted as the starting point of the decomposition.

A difficulty is encountered if it is supposed that decomposition occurs uniformly throughout the lattice. It would then be necessary to postulate the reaction

$$ClO_4^- \rightarrow ClO_4^{-*} \qquad [2]$$

followed by

$$ClO_4^{-*} \rightarrow ClO_3^- + O \qquad [3]$$

occurring at an ordinary lattice site, i.e. away from imperfections. The oxygen could not easily escape from the point where it was formed. Even if [3] could take place, it is hardly reasonable to suppose that an arrangement consisting of a chlorate ion with an oxygen atom held close to it by the surrounding lattice could persist in this state without reverting to a perchlorate ion, since all our knowledge indicates that the necessary electronic rearrangement would occur instantly and spontaneously in such circumstances. Moreover, in view of the large size of the oxygen atom and the low temperature, one cannot reasonably assume that oxygen atoms could diffuse away from the point where they were formed at an appreciable rate. The alternative is to postulate that decomposition takes place at lattice imperfections and surfaces. Here we are faced with an apparent difficulty in explaining the relatively efficient energy utilization in the reaction. Only a minute fraction of the primary excitation can occur in the neighborhood of imperfections and surfaces, whereas the energy utilization observed requires that at least one third the ClO_4^- ions excited decompose.

The solution of this problem is probably to be found in the "exciton" theory first advanced by Frenkel (5). According to this, a point of electronic excitation, or "exciton", in a crystal lattice can travel considerable distances through the lattice by successive excitation and de-excitation of adjacent ions: alternatively, the excitation cannot a priori be regarded as localized at any particular lattice point. We can postulate that the excitons formed in the potassium perchlorate lattice travel until they reach an imperfection (most probably an internal crack or edge dislocation), at which point room is available for the excited ClO_4^- to dissociate. Hence chloride and chlorate would accumulate in internal cracks, weakening the crystal structure. The oxygen gas formed in the same places would build up a pressure. Eventually these combined factors would lead to violent rupture of the crystal, as observed.

According to this explanation, blocks of chloride and chlorate lattices, or a mixture of the two, should be built up in limited regions inside the potassium perchlorate crystal and on its surface, probably at first in a fragmentary condition, as long as they are only a few ions thick. On account of the closer packing of ions in potassium chloride, as compared with potassium chlorate, and the resulting higher lattice energy, an arrangement in which the potassium chloride and potassium chlorate lattices are entirely separate would be more stable than a potassium chlorate lattice in which ClO_3^- ions were replaced at intervals by Cl^- ions. Probably, therefore, chloride and chlorate would accumulate at imperfections and surfaces in the form of blocks of pure chloride and pure chlorate.

Since only the exact energy of excitation of a ClO_4^- ion could easily be transferred to adjacent ClO_4^- ions, only excitation originally produced in ClO_4^- can be effective in bringing about decomposition of ClO_4^- at lattice imperfections and surfaces. Thus the rate of decomposition of ClO_4^- should be proportional to the total amount of ClO_4^- present, and independent of the other substances (neglecting minor factors). The same is true of the decomposition of ClO_3^-. The experimentally observed first order decompositions are therefore in agreement with the hypothesis just advanced. The increase in the rate of chloride formation with the break-up of potassium perchlorate crystals is probably connected in some way with the sudden increase of free surface, which it is reasonable to suppose would encourage dissociation of ClO_4^- to Cl^- rather than to ClO_3^-, since more room would be available for escape of oxygen atoms. The same "explanation" can be given for the fact that ClO_3^- as formed in the perchlorate decomposes almost entirely to Cl^-, whereas in large crystals of potassium chlorate, ClO^- and ClO_2^- are also formed in considerable amounts. It must be admitted, however, that there are objections to this description of the process which can hardly be answered without further experimental work.

ACKNOWLEDGMENTS

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NOTE

THE PYROLYSIS OF CALCIUM SALTS OF CARBOXYLIC ACIDS

By C. C. Lee and J. W. T. Spinks

Recently, Bell and Reed (1) reported that the C^{13} content of the carbonyl-carbon atom of the acetaldehyde obtained in the pyrolysis of a mixture of barium acetate, enriched with C^{13} in the carboxyl group, and barium formate is approximately normal. This requires the fission of the carbon–carbon bond in the acetate. A free radical mechanism was suggested to interpret the results. A similar tracer technique has been applied in our laboratory in the study of such pyrolyses.

Calcium acetate labelled with C^{14} in the carboxyl group and an equimolar quantity of unlabelled calcium benzoate, *p*-toluate, phenylacetate, or *n*-valerate were dissolved in water, evaporated to dryness to give an intimate mixture, and then dry distilled. In each experiment, the liquid product was taken up in ether, thoroughly washed with water to remove acetone, dried over anhydrous sodium sulphate, and treated with decolorizing charcoal. The ether was then removed and the residue fractionated. The unsymmetrical ketones obtained were converted to the corresponding semicarbazones and their radioactivity determined. The results (Table I) indicate that the fission of the carbon–carbon

TABLE I

Radioactivity data

Semicarbazones of unsymmetrical ketones obtained by pyrolysis of mixed calcium salts

Compound	Observed activity,[a] counts/min.		Activity/millimole,[b] counts/min.		% of acetate activity in ketone	
	Run I	Run II	Run I	Run II	Run I	Run II
CH_3COONa	3390	3366	278	276		
$C_6H_5(CH_3)CNNHCONH_2$	22.2	22.8	3.93	4.03	1.4	1.5
p-$CH_3C_6H_4(CH_3)CNNHCONH_2$	19.2	22.8	3.67	4.36	1.3	1.6
$C_6H_5CH_2(CH_3)CNNHCONH_2$	484	483	92.5	92.3	33.3	33.4
$CH_3(CH_2)_2(CH_3)CNNHCONH_2$	335	327	53.0	51.7	19.1	18.7

[a] *At "infinite thickness".*
[b] *Observed activity × molecular weight × 10⁻³.*

bond in the acetate accounts for the formation of almost all of the acetophenone and *p*-methylacetophenone, about four fifths of the *n*-amyl methyl ketone, and about two thirds of the benzyl methyl ketone.

The above findings render unsatisfactory any mechanism involving heterolytic cleavage of the carbon–carbon bond since the predominance of a carbonium ion or a carbanion of the CH_3^+ or CH_3^- type is very unlikely. A mechanism involving an aldol type of reaction, as suggested by Miller, Cook, and Whitmore (3), is also questionable. Aside from the fact that an aldol condensation between salts of carboxylic acids is improbable, no aldol condensation can account for the formation of diaryl ketones from the pyrolysis of salts of aromatic acids. A free radical mechanism as suggested by Bell and Reed (1) remains attractive. In the formation of acetophenone, for example, the reaction sequence may be written:

Initiation	$CH_3COOM \rightarrow CH_3\cdot + \cdot COOM \qquad M = \frac{1}{2}\,Ca$
Chain continuation	$CH_3\cdot + C_6H_5COOM \rightarrow CH_3COC_6H_5 + MO\cdot$
	$CH_3COOM + MO\cdot \rightarrow CH_3\cdot + M_2CO_3$
Termination	$2CH_3\cdot \rightarrow CH_3CH_3$, or $CH_4 + CH_2$: etc.
	$2\,MO\cdot \rightarrow (MO)_2$
	$MO\cdot + \cdot COOM \rightarrow M_2CO_3$

Clarification of certain questionable aspects is still needed before the free radical chain can be accepted as the sole mechanism. In the homolytic cleavage of the carbon–carbon bond, other things being equal, one would expect the benzyl radical to be more readily formed than the methyl radical (5). However, in the formation of benzyl methyl ketone, if only the radical mechanism operates, our results would indicate a two-thirds predominance of the methyl over the benzyl free radical. The detailed study of the pyrolysis of trimethylacetic acid by Miller *et al.* (3) certainly renders impossible any satisfactory explanation of the multitude of products without assuming the presence of some free radicals. To explain, on a free radical basis, the formation of the main product of the reaction, the unsymmetrical *t*-butyl *iso*-butyl ketone, a rearrangement from a tertiary carbon radical (*t*-butyl radical) to a primary carbon radical (*iso*-butyl radical) is necessary. Established rearrangements involving free radicals (6,7), however, indicate an opposite trend in that primary radicals tend to rearrange to the tertiary state.

A polar mechanism operating in conjunction with one of the free radical type may be considered. The first step may be the formation of an acyl carbonium ion followed by an S_E2 type of decarboxylation (2,4) with the acyl carbonium ion acting as the electrophilic component.

$$R{-}COOM \rightarrow R{-}C^+{=}O + MO^-$$

$$R{-}C^+{=}O + R'{-}COOM \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}R' + M^+ + CO_2$$

where R and R′ may be the same or different, aliphatic or aromatic, and M is a metal such as calcium or barium, etc. When R is aromatic, resonance of the type

$$-C^+{=}O \leftrightarrow +\!=C{=}O \leftrightarrow +\!=C{=}O$$

would greatly increase the probability of its formation over that of the methyl acyl carbonium ion, $CH_3-C^+=O$, accounting for the exclusive carbon–carbon cleavage of the acetate when it is pyrolyzed with benzoate or *p*-toluate. However, on the basis of hyperconjugation, $CH_3-C^+=O$ would be expected to have a greater probability of formation than either $C_6H_5CH_2-C^+=O$ or $CH_3(CH_2)_3-C^+=O$. Resonance interpretations alone thus fail to account for the preferred cleavage of the carbon–carbon bond of acetate in the pyrolytic production of benzyl methyl ketone and *n*-amyl methyl ketone. A possibility may be that this pyrolysis may proceed through both polar and free radical mechanisms, the observed results being the composite of the two.

A two-step mechanism in which an acyl carbonium ion is produced by a fairly rapid reversible process followed by a rate-controlling S_E2 displacement may also be considered.

$$R-COOM \rightleftarrows R-C^+=O + MO^-$$

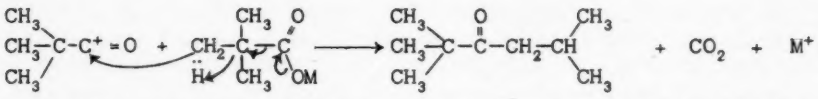
$$R-C^+=O + R'-COOM \xrightarrow{\text{slow}} R-\overset{\overset{O}{\|}}{C}-R' + M^+ + CO_2$$

Considering first the pyrolysis of calcium acetate with calcium benzoate or toluate, it is seen that the S_E2 displacement of $C_6H_5-C^+=O$ on calcium acetate would involve a backside attack on the methyl carbon with Walden inversion, whereas the displacement of $CH_3-C^+=O$ on calcium benzoate or toluate would of necessity proceed by a frontal attack on a carbon of the nucleus. These two reactions, being quite different in nature, might be expected to proceed at very different rates, and this, rather than the relative probability of formation of the two onium ions in the first step, might account for the observed exclusive carbon–carbon cleavage in acetate.

The preferred cleavage of the carbon–carbon bond of acetate in the pyrolysis with phenylacetate and *n*-valerate may be explained in terms of this mechanism on the basis of a difference in the steric factor. The attack of $CH_3-C^+=O$ on phenylacetate or *n*-valerate would be expected to have a lower entropy of activation than the alternative process involving the attack of $C_6H_5CH_2-C^+=O$ or $CH_3(CH_2)_3-C^+=O$ on acetate.

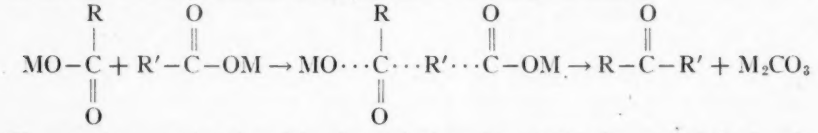
Finally, the difference in the extent of carbon–carbon cleavage of acetate in its pyrolysis with phenylacetate and *n*-valerate could be attributed to a difference in activation energy. The cleavage of the carbon–carbon bond in phenylacetate would be expected to require a lower energy of activation then carbon–carbon cleavage in *n*-valerate since this bond in phenylacetate is one carbon atom removed from the aromatic nucleus. Moreover, the observation of Bell and Reed (1) might be similarly explained for the activation energy required for carbon–carbon cleavage in barium acetate should be lower than that for carbon–hydrogen cleavage in barium formate.

Steric considerations would also render an interpretation for the formation of the major product in the pyrolysis of trimethylacetic acid (3). The *t*-butyl group may hinder the approach of the acyl carbonium ion in the S_E2 decarboxylation. A carbon atom β to the carboxyl instead of the α-carbon atom is then attacked.



The polar mechanism involving an acyl carbonium ion may further afford at least one explanation for the well-known fact that in the ketonic pyrolysis of salts of carboxylic acids, lithium, barium, and calcium salts proceed more smoothly than sodium and potassium salts. Relatively speaking, metals of the first group have a greater affinity for electrons than those of the second. The splitting off of MO^-, and hence the production of the acyl carbonium ion, is thus favored where M is the less basic metals.

Possibly, one may criticize the mechanism outlined on the basis that the formation of an onium ion usually is slow compared to its subsequent reaction to give the final product. Instead of the two-stage mechanism, the decarboxylation reaction might conceivably proceed in one step as follows:



The reaction may involve either heterolytic or homolytic cleavage of the bonds concerned. The arguments presented above, based on the two-step mechanism, should apply equally well to the one-step interpretation.

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